Homogeneous Carbon Monoxide Reduction - Catalyst Design Strategies

Thesis by

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In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1983

(submitted May 24, 1983)

To my Parents

and

to Cathy

ACKNOWLEDGMENTS

I would like to thank Bob Grubbs for giving me the freedom to pursue a delightful combination of fruitful avenues and red herrings during my tenure at Caltech. Thanks also to Bob for a certain 1974 cabernet and a mysterious bag of chocolate chip cookies. Fred Anson proved an invaluable aid in the course of the electrochemical investigations, and I am most grateful to him for this help. Special thanks are also due to Terry Collins, a good friend as well as valuable scientific associate, and to the other members of the faculty who expressed interest in various phases of my research, Harry Gray, Dave Evans, and John Bercaw (who actually listened to my entire porphyrin seminar my first year here). The Fannie and John Hertz Foundation made all this possible, and I am pleased to acknowledge their financial support.

I won't mention names for fear of leaving some out, but thanks to all those members of the Grubbs' group past and present who made my stay at Caltech more enjoyable, and to those in the Anson, Bercaw, and Collins groups who, through either work or play, did the same. Special thanks to Eric Moore, Mike Steigerwald, and Brian Willett for their friendship. Dot Lloyd has done a wonderful job typing and illustrating this thesis, and I am forever indebted to her. The San Gabriels, the biting flies of Fox Mountain and Condor Peak, and the rattlesnakes of Iron Mountain also contributed greatly to my career at Caltech.

Finally, my heartfelt thanks are given to my parents for their support and encouragement, and to my wife Cathy for her love and understanding, without which this work would not have been possible.

ABSTRACT

A new approach to the activation of carbon monoxide toward homogeneous reduction by hydrogen is presented. Attack at transition metal bound carbon monoxide by nucleophiles generates anionic carbene complexes; hydrogenation of such complexes should give rise to products derived from reduced carbon monoxide. Model stoichiometric reactions using lithium dimethylamide as the activating nucleophile and various binary transition metal carbonyls have been found to give rise to varying amounts of methanol, dimethylformamide (DMF), and trimethylamine, products derived from reduction of carbon monoxide (as confirmed by carbon-13 labeling), under exceptionally mild conditions [35 psi H_2, 130 °C, tetrahydrofuran or hexamethylphosphoric triamide (HMPA) solvent]. In the $Cr(CO)_6/LiNMe_2$ system in HMPA, trimethylamine appears to be formed by hydrogenation of the primary product DMF by a chromium carbonyl hydride anion. In support of this, the pentacarbonyl chromium hydride anion, $(CO)_5CrH^-$, has been found to quantitatively reduce N,N-dialkylamides to the corresponding amines under the above hydrogenation conditions.

Nucleophiles weaker than $LiNMe_2$ do not give rise to the desired activation of carbon monoxide for homogeneous reduction. Attempts to drive unfavorable equilibria through the use of bifunctional nucleophiles are reported. Intramolecular delivery of weaker nucleophiles has also been investigated in a series of functionalized arene chromium tricarbonyl complexes; no sign of the desired nucleophilic attack at carbon monoxide is

obtained, though interesting reductive degradations and couplings of arenes are observed.

The electrochemical oxidation of a series of arene chromium and arene tungsten tricarbonyl complexes has been examined. Studies regarding the oxidatively-promoted decomposition of the chromium complexes are reported. Extension of these studies to the tungsten analogs has led to the observation of metal coordination sphere expansion upon one-electron oxidation, an observation of fundamental significance with regards to recent reports of dramatic reaction rate enhancements in odd-electron organometallic systems. The relationship of coordination sphere expansion to these and other problems of current mechanistic organometallic chemical interest, including the oxidative instability of arene chromium tricarbonyl complexes, is discussed.

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CHAPTER I

Intermolecular Nucleophilic Activation of Carbon Monoxide for Homogeneous Reduction

Introduction

The Arab oil embargo of 1973, coupled with the spiraling price of crude oil and the desire for energy self-sufficiency, has led to dramatically increased interest in alternative fuel sources. The conversion of synthesis gas -- a mixture of carbon monoxide and hydrogen generated from coal through combustion in the presence of oxygen and water -- to fuel-type products is one particularly attractive source. The heterogeneous catalysis of this conversion, the so-called Fischer-Tropsch synthesis, has been investigated in great detail,[1] beginning with the pioneering work of Fischer and Tropsch[2] in 1923. Though fuels are readily accessible via the heterogeneous Fischer-Tropsch synthesis -- Germany's war efforts in the 1940's were greatly aided by fuels derived from the synthesis[5] -- currently only South Africa is seriously using the process in its drive for energy independence.[6] The chief objections to the Fischer-Tropsch synthesis as a viable source of fuel concern its lack of selectivity; typically, mixtures of alkanes, alkenes, alcohols, ketones, aldehydes, and acids, in varying proportions, are obtained.[7] Several recent reports claiming moderate[8-12] to high[13-15] selectivity in heterogeneous Fischer-Tropsch reactions have appeared, but, in general, it is agreed that the best possible entry into selectivity will be through the use of homogeneous analogues of the Fischer-Tropsch reaction. Whereas the detailed nature of the catalyst in the heterogeneously catalyzed reactions is only poorly understood, the clearly-defined (for the most part) nature of soluble metal species, coupled with the basic knowledge of reaction pathways of such soluble species, suggests that the use of soluble metal systems to catalyze homogeneous Fischer-Tropsch

type reactions should lead to enhanced selectivity.

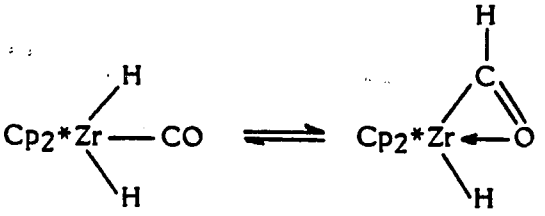
Though the homogeneous hydrogenation of carbon monoxide has only recently been achieved,[16,17] the literature of the past few years abounds with reports of such reactions, in which transition metal bound carbon monoxide is reduced by hydrogen. An examination of these reports suggests that simple bonding of carbon monoxide to a transition metal is not sufficient to give rise to reactions with hydrogen. Instead, bound carbon monoxide must be further activated before its reactions with hydrogen occur. This activation has been achieved in several ways: coordination of Lewis acids at the carbonyl oxygen[17-21]

$$Ir_4(CO)_{12} \xrightarrow{AlCl_3} [(CO)_{11}Ir_4\text{-}C\equiv O\cdots AlCl_3] \xrightarrow{H_2} CH_4 + C_2H_6 \qquad \text{(Ref. 17)}$$

bonding to a metal cluster[22-25] (which can serve as a source or sink of electrons)

$$Os_3(CO)_{12} \xrightarrow{H_2/CO} CH_4 \qquad \text{(Ref. 23)}$$

and inter- or intramolecular donation of hydride to the carbonyl carbon.[26-32]



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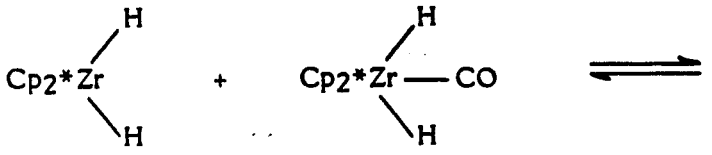

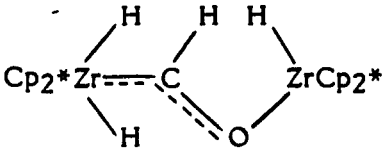

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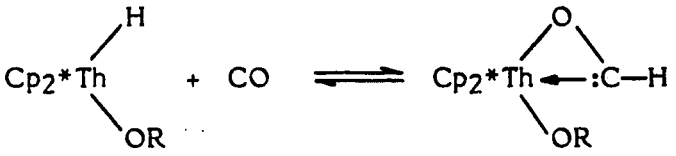
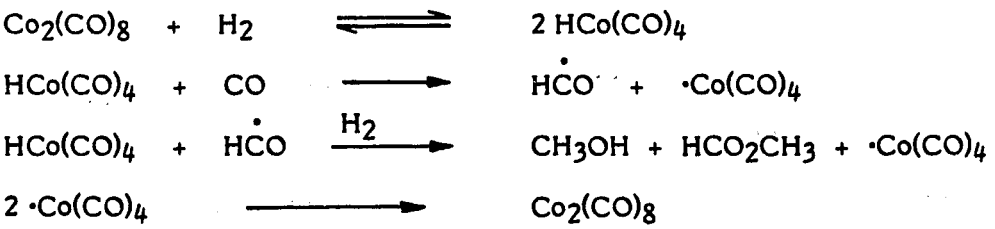


(Ref. 32)

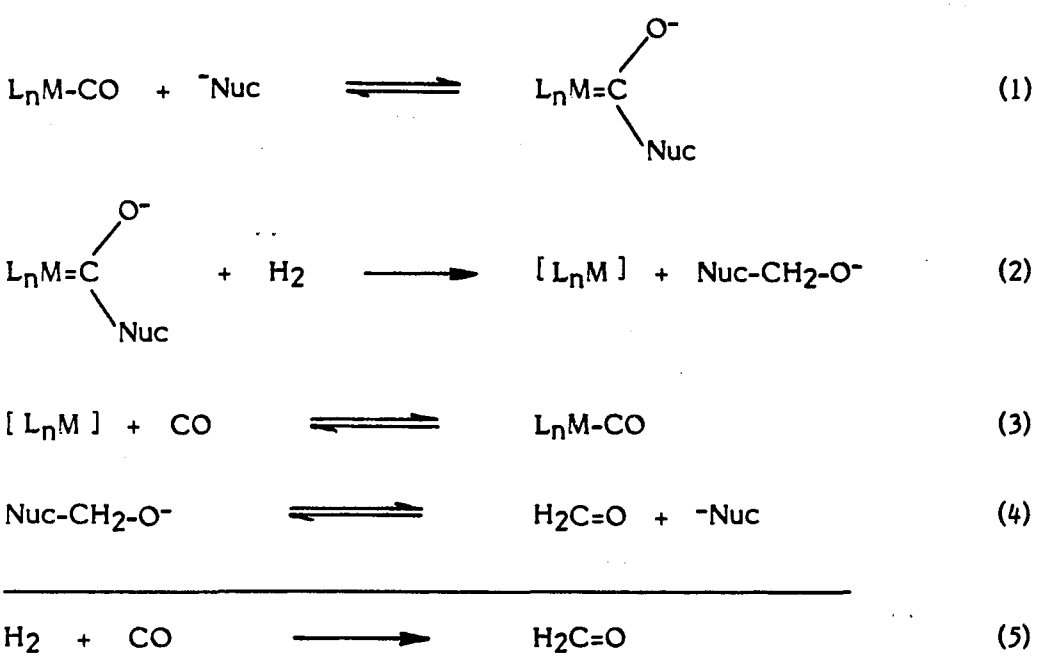
A potential complication in this classification scheme[33] is suggested by the observations of Rathke and Feder,[34] who propose the existence of radical pathways in homogeneous carbon monoxide hydrogenation reactions.



In addition, some catalytic systems combine carbon monoxide activation approaches -- for example, Muetterties' cluster systems in aluminum halide

melts[17] involve both cluster and Lewis acid activation. In general, though, reported homogeneously catalyzed hydrogenations of carbon monoxide may be readily catalogued according to the scheme.

Based on known organometallic reactions, a nucleophile catalyzed, transition metal mediated homogeneous hydrogenation of carbon monoxide may be proposed.[38]



Before considering the steps of the proposed mechanism in detail, a comment on the overall stoichiometry of the catalyzed reaction (eq. 5) is in order. The reaction, as written, is thermodynamically unfavorable ($\Delta G°_{298}$ = +5.5 kcal/mol; Table 1). Formaldehyde, however, is known to undergo a wide array of condensations and polymerizations[43] (vide infra) which are far downhill thermodynamically (Table 1). Thus, if the catalyzed reaction of hydrogen and carbon monoxide is proposed to yield not free formaldehyde, but

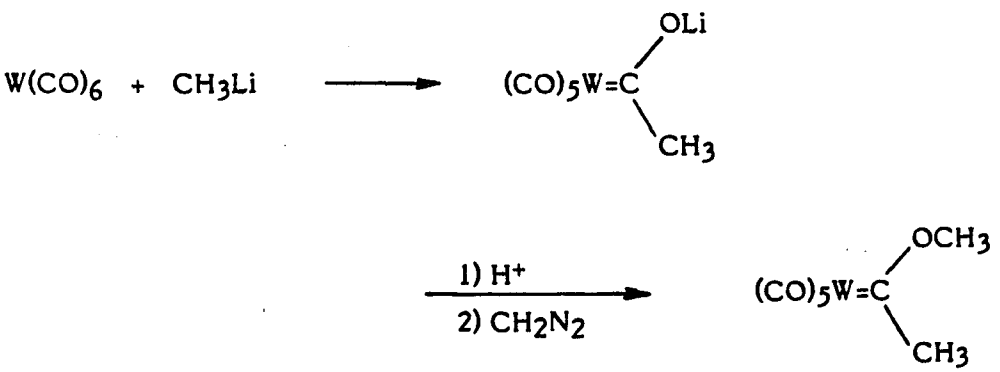
Table 1. Relevant Thermodynamic Parameters*

Compound	State	ΔH°_{f298} (kcal/mol)	S°_{298} (cal/mol-K)	ΔG°_{f298} (kcal/mol)
H_2	G	0	0	0
CO	G	-26.42	47.30	-32.81
CO_2	G	-94.05	51.07	-94.26
H_2O	G	-57.80	45.11	-54.64
CH_2O	G	-27.70	52.29	-26.27
$(CH_2O)_n$	S	-40.20	--	--
CH_3OH	G	-48.08	57.29	-38.84
CH_4	G	-17.89	44.52	-12.15
C_2H_4	G	12.50	52.45	16.28
C_2H_6	G	-20.24	54.85	-7.87
OHCCHO	L	-83.7	--	--
$HOCH_2CH_2OH$	L	-108.73	39.9	-77.29
$HOCH_2CH_2OH$	G	-93.05	77.33	-72.77
$HOCH_2\underset{\displaystyle OH}{\underset{\vert}{C}}HCH_2OH$	L	-159.8	48.87	-114.02

*From Reference 37.

rather complexed formaldehyde, remaining in contact with the metal and/or the nucleophile, and this complexed formaldehyde then reacts further[44] to produce formaldehyde polymers or condensation products, then the net reaction will be downhill, without the need to pass through the high energy intermediate, free formaldehyde.[48] This rationalization, however, may prove unnecessary -- the production of formaldehyde is proposed by analogy with the hydrogenation examined by Casey and Neumann[49] (vide infra), but experimentally other products may well arise; formaldehyde is proposed above only to allow the simplest possible presentation of the catalytic scheme.

The first step of the proposed catalytic sequence, nucleophilic attack at the carbon atom of transition metal bound carbon monoxide (eq. 1) has abundant precedent. Since Fischer's first report[50] of the formation of a carbene complex from such a reaction



many similar syntheses have been reported.[51] Of relevance to the proposed mechanism, however, are those reactions in which the bond between the carbonyl carbon and the nucleophile is not formed irreversibly. Numerous

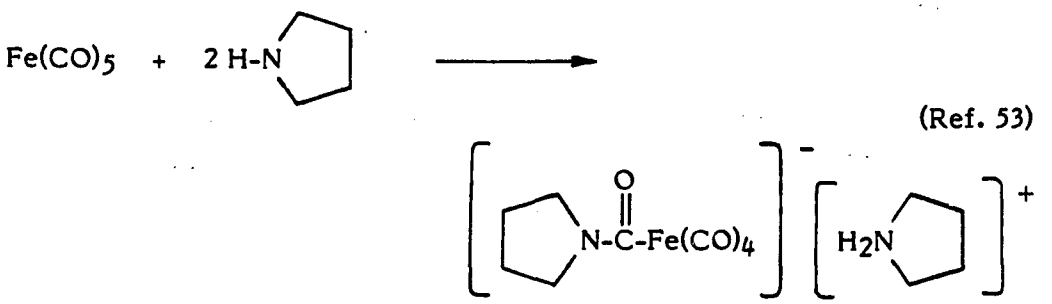
examples of reactions of this type are also available; an incomplete but revealing set of such reactions is presented in Table 2. In general, cationic carbonyl complexes are more susceptible to nucleophilic attack at carbonyl carbon than are neutral carbonyl complexes.

$$Cr(CO)_6 + H_2{}^{18}O \longrightarrow \text{no reaction}$$

$$[Mn(CO)_6]^+ + H_2{}^{18}O \longrightarrow [Mn(CO)_n(C^{18}O)_{6-n}]^+$$

(Ref. 52)

Even neutral carbonyl complexes are readily attacked by anionic nucleophiles, though, and in fact certain neutral carbonyls even display analogous reactivity with neutral nucleophiles.



(Ref. 53)

The hydrogenation of a "Fischer type" carbene complex (eq. 2) has been examined by Casey and Neumann.[49]

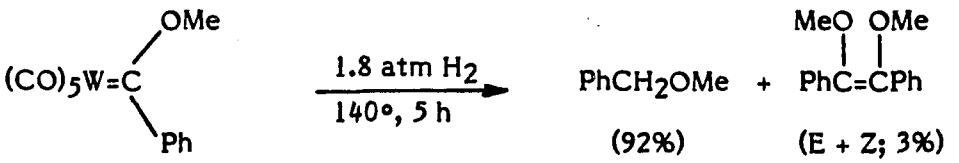


Table 2. Nucleophilic Reactions at Bound Carbon Monoxide.

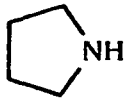
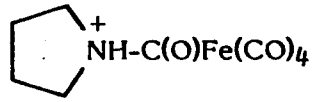
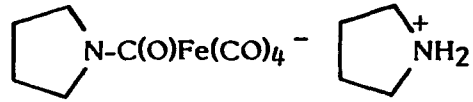
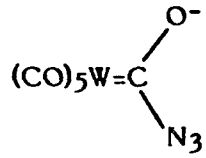
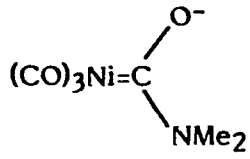
Metal System	Nucleophile	Intermediate	Product	Ref.
$Fe(CO)_5$				53
$Fe(CO)_5$	Br_2	$BrC(O)Fe(CO)_4 \cdot Br$	cis-$Fe(CO)_4Br_2$	109
$W(CO)_6$	N_3^-		$(CO)_5W(NCO)^- + N_2$	110
$Cr(CO)_6$	X^-	$(CO)_5Cr=C(O^-)(X)$	$(CO)_5CrX^- + CO$	111
$W(CO)_6$	Me_2P^-	--	cis-$(CO)_4W\ C(O^-)(PMe_2)_2$	65a
$Ni(CO)_4$	Me_2N^-	--		112

Table 2. Continued

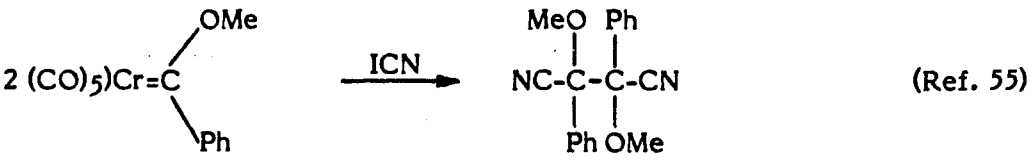
Metal System	Nucleophile	Intermediate	Product	Ref.
$CpFe(CO)_3^+$	H_2NNH_2	$Cp(CO)_2FeC(O)NHNH_2$	$Cp(CO)_2Fe(NCO) + NH_3$	113
$Re(CO)_6^+$	NH_3	$(CO)_4(NH_3)ReC(O)NH_2$	$HRe(CO)_5 + H_2NC(O)NH_2 + NH_4^+$	114
$Pt(SCN)(CO)(PPh_3)_2^+$	MeOH	--	$Pt(SCN)(CO_2Me)(PPh_3)_2$	115
$Ir(CO)(dmpe)_2^{+*}$	MeOH	--	$IrH(CO_2Me)(dmpe)_2^+$	116
$Re(CO)_6^+$	MeO^-	--	$(CO)_5ReCO_2Me$	117
$Ir(CO)_2(CS)(PPh_3)_2^+$	MeO^-	--	$Ir(CO_2Me)(CO)(CS)(PPh_3)_2$	118
$CpFe(CO)_2(CS)^+$	MeO^-	--	$Cp(CO)_2FeC(S)OMe$	119

*dmpe = $Me_2PCH_2CH_2PMe_2$

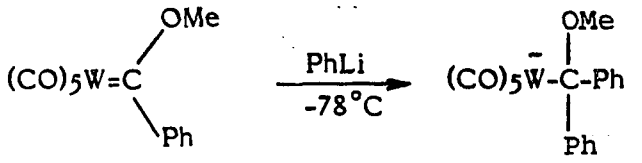
Though the mechanism for the hydrogenation is unknown, the temperature required for the reaction suggests that carbon monoxide must dissociate before hydrogenation can occur. A moderate yield of $W(CO)_6$ was isolated from the reaction mixture, suggesting the metal fragment left after the carbene ligand is lost to hydrogenation may be $W(CO)_5$, which then scavenges carbon monoxide from other carbonyl-containing fragments. The reaction proposed in equation 2, then, has precedent, and the fact that the metal fragment produced may be recycled to the starting carbonyl (eq. 3) bodes well for the proposed catalytic nature of the mechanism.

The final proposed reaction (eq. 4) is merely an equilibrium between a carbonyl-containing organic molecule and a base. Even if this equilibrium lies far to the left, it should be possible to drive it to the right by removing organic product (perhaps via distillation or follow-up reaction) as it is formed, thus freeing the activating nucleophile and completing the proposed catalytic cycle.

The proposed nucleophile catalyzed, transition metal mediated hydrogenation of carbon monoxide has been presented in the simplest form possible. As such, the anticipated product is suggested to be formaldehyde. Given the initial formation of a "Fischer type" carbene complex, however, other reaction pathways than simple hydrogenation are potentially available.[54] For example, carbon nucleophiles can attack at the carbene carbon.



(Ref. 55)



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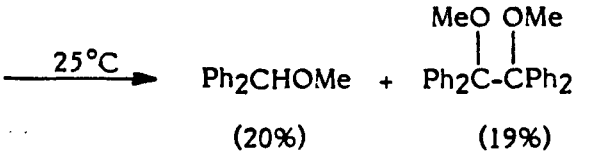
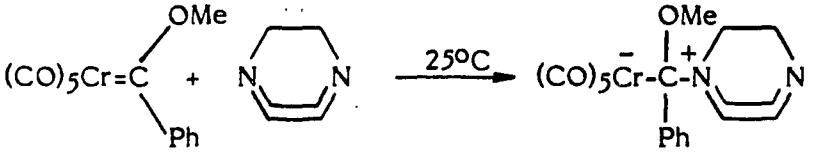
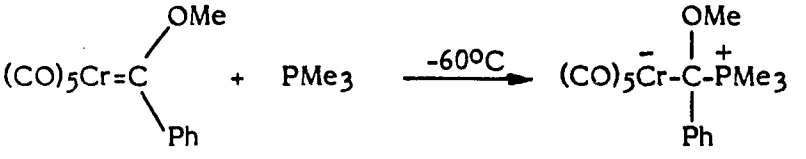


Tertiary amines and phosphines also attack the carbene carbon, generating ylid complexes.

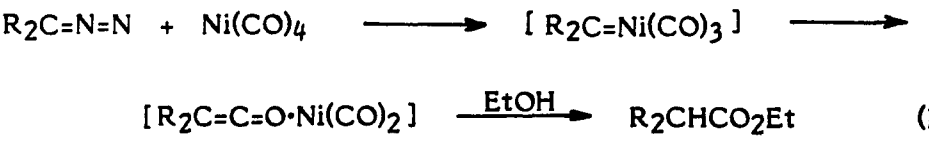


(Ref. 57)



(Ref. 58)

Closely related to the latter reaction is the reaction of carbon monoxide with carbene complexes, proposed to generate ketene intermediates.



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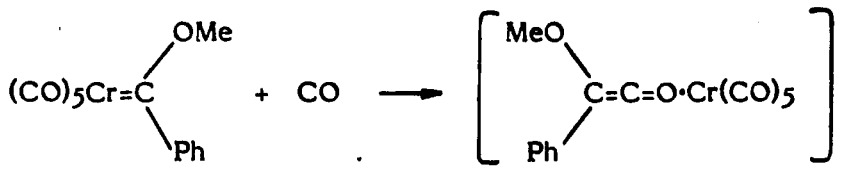

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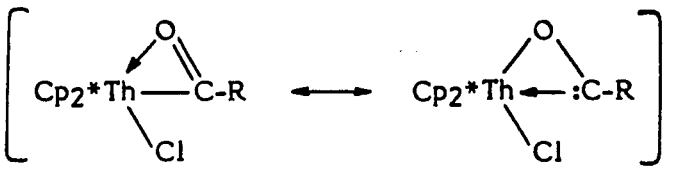

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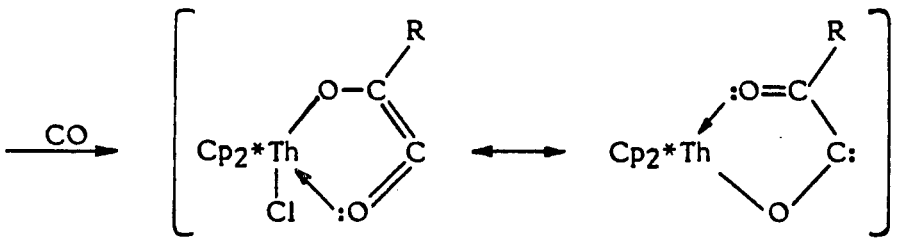
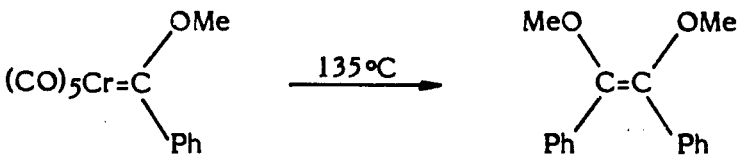
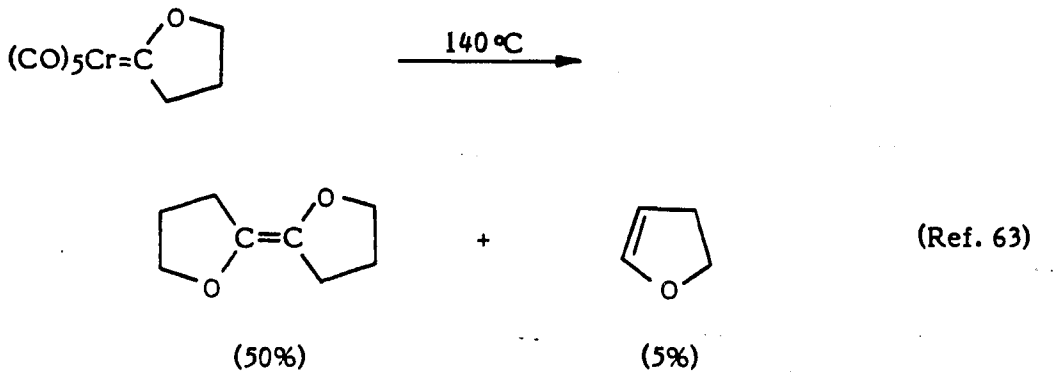


A final reaction of relevance to the proposed catalytic cycle is the thermal decomposition of carbene complexes,[54] which has been shown to yield dimerization products.



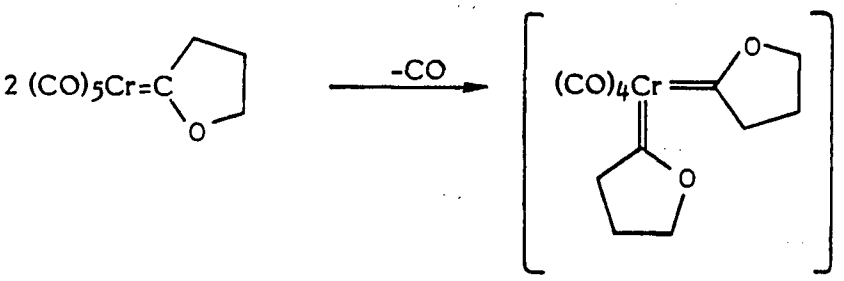
(Ref. 62)

(60%; E/Z = 2)



(Ref. 63)

An examination of the latter reaction demonstrated second order dependence on starting complex concentration, inhibition by external carbon monoxide, and more rapid carbon monoxide exchange than carbene dimerization, by which formation of an intermediate cis biscarbene complex was proposed.[63,64]



Nucleophilic activation of transition metal bound carbon monoxide, then, has the potential to lead to a range of functionalized organic products.

Results and Discussion

Preliminary investigations by Stewart[66] into the reactions of alkoxides with transition metal carbonyl complexes, under hydrogenation conditions

analogous to those used by Casey,[49] were distressing, in that only traces of products were observed

$$M(CO)_n + RO^- \xrightarrow{H_2/CO} CH_4 \text{ (trace)}$$

and, in addition, the observed product was not an oxygenate. Based on carbon-13 nuclear magnetic resonance (NMR) evidence, the reason for the apparent failure of these reactions was suggested to be a highly unfavorable equilibrium constant for the initial formation of a Fischer type carbene complex.

$$M(CO)_n + RO^- \rightleftharpoons (CO)_{n-1}M{=}C(O^-)(OR)$$

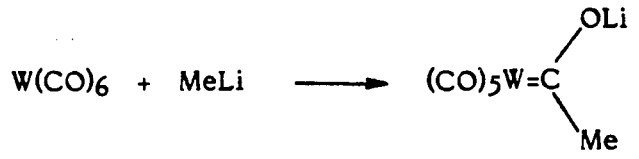
This proposal has been borne out by Fischer's report[67] of isolation of such a carbene complex (after alkylation) in only very low yield.

$$Cr(CO)_6 + EtO^- \longrightarrow \xrightarrow{Et_3OBF_4} (CO)_5Cr{=}C(OEt)(OEt) \quad (0.08\%)$$

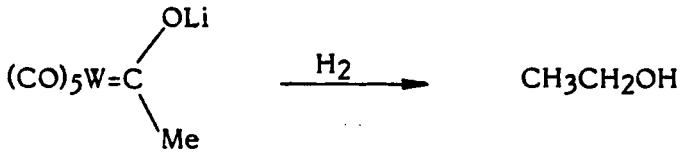
Several approaches to overcoming this unfavorable equilibrium are evident. Intramolecular delivery of the alkoxide (or other nucleophilic moiety) is one particularly attractive alternative (Chapter II). A rather less elegant but

potentially equally effective approach involves the use of better nucleophiles.

The reaction between tungsten hexacarbonyl and methyllithium leads to the anionic carbene complex in high yield.[50]



When this complex was stirred with hydrogen under the hydrogenation conditions used by Casey (35 psi H_2, 130°C, tetrahydrofuran (THF) solution), a greater than 50% yield of ethanol (by gas chromatography) was obtained.



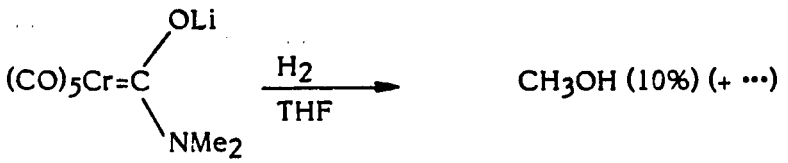
The metal fragment has not been identified but, by analogy with Casey's work, is presumed to be $W(CO)_5$, which decomposes to produce the insoluble residue observed in the hydrogenation reaction. A simple carbon nucleophile such as CH_3^- is not of interest with regards to the proposed catalytic cycle, of course, as once the carbon-carbon bond has formed, it is not expected to break (under ordinary reaction conditions), and the nucleophile will be lost. However, the results of this experiment do suggest that interesting products can indeed be obtained from the hydrogenation of anionic Fischer type carbene complexes.

The reaction between group 6B metal hexacarbonyls and lithium

dialkylamides also gives rise to high yields of anionic carbene complexes.[68,69]

1

When the chromium complex 1 was hydrogenated, a low yield of methanol was obtained.



Repetition of the experiment using carbon-13 labeled $Cr(CO)_6$ led to product methanol enriched in carbon-13 to the same extent as the starting $Cr(CO)_6$. Methanol was also obtained when a mixture of $Cr(CO)_6$ and lithium dimethylamide in THF was treated with hydrogen, so isolation of the intermediate anionic carbene complex is not necessary. The carbon-13 labeling study proves that the product methanol is derived from carbon monoxide; however, the mechanism of formation of methanol is completely unknown. The reaction mixture did not remain homogeneous -- a dark solid was precipitated -- and methanol could possibly be produced by a heterogeneously catalyzed reaction of carbon monoxide and hydrogen. Production of methanol from the direct hydrogenation of the carbene

complex is a second possibility. Finally, the carbene complex, when hydrogenated, may have produced formaldehyde, as proposed in the "simplistic" catalytic scheme (eqs. 1-5); product formaldehyde could then have undergone further reactions, producing methanol and/or other products. The latter possibility, follow-up reactions of primary product formaldehyde, is of sufficient relevance to the catalytic proposal (as well as to thermodynamic arguments regarding the feasibility of the proposed catalytic cycle -- vide supra) to merit a full discussion of the various possible reactions of formaldehyde under the reaction conditions.

Simple hydrogenation of formaldehyde to methanol could presumably occur in the presence of hydrogen and a transition metal.[70] More interesting, perhaps, is the possibility of formation of multicarbon species through the hydroformylation of formaldehyde,[70-72] a process proposed[70] to proceed via a mechanism analogous to that for olefin hydroformylation[73,74] (Figure 1). Furthermore, formaldehyde in the presence of strong bases at elevated temperatures is prone to a range of reactions.[43] Condensation to produce polyoxymethylenes of varying chain lengths readily occurs.

$$n CH_2O \rightleftharpoons (CH_2O)_n$$

These polymerizations are, for the most part, freely reversible, so formaldehyde is not permanently lost in such reactions. On the other hand, bases also catalyze the Cannizzaro reaction of formaldehyde, producing methanol and formic acid, by which formaldehyde is irreversibly lost. (In fact, preliminary evidence[75] suggests that formic acid may indeed be a product of

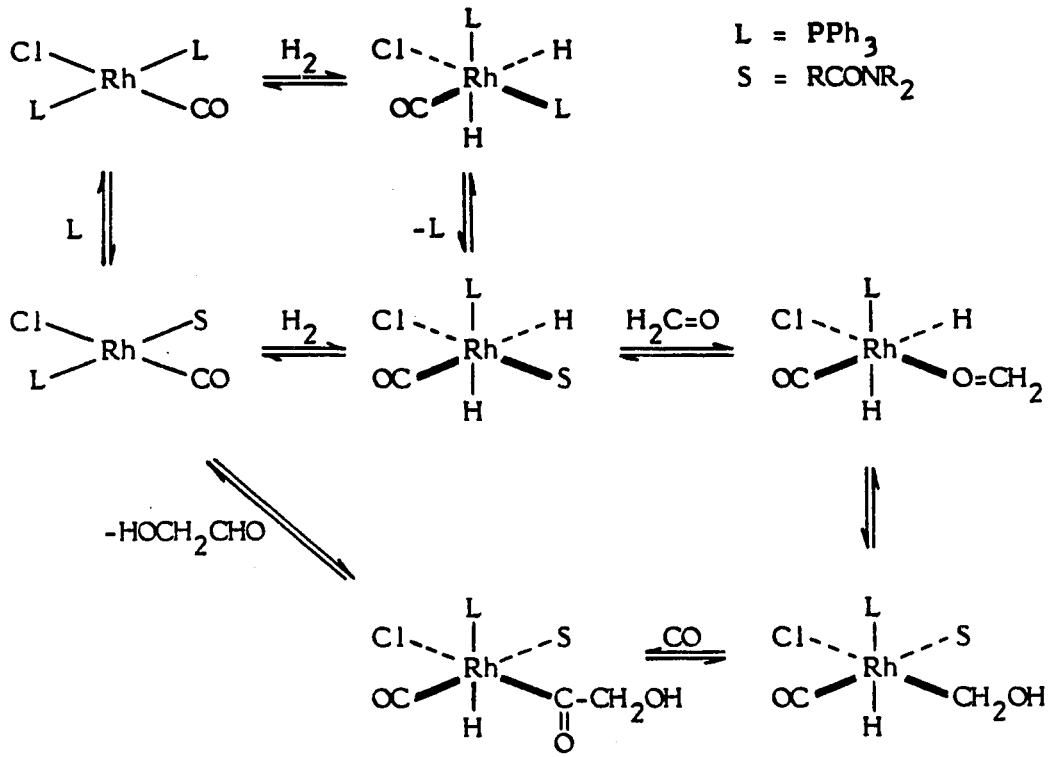


Figure 1. Formaldehyde hydroformylation.

the $Cr(CO)_6/LiNMe_2/H_2$ reaction in THF). In addition, the self-condensation of formaldehyde to sugar-type products, the so-called formose reaction, is base catalyzed. Though the detailed mechanism of this autocatalytic reaction is not fully understood, there is general agreement on an initial catalyzed condensation of two formaldehyde molecules to produce glycolaldehyde (either free or complexed), which then undergoes a combination of aldol condensations, cross-Cannizzaro reactions with formaldehyde, and Lobry de Brun-van Eckstein rearrangements to yield ultimately the thirty to forty observed two to seven carbon (primarily) sugars and polyols as products[76,77] (Figure 2). Indeed, the reaction of formaldehyde

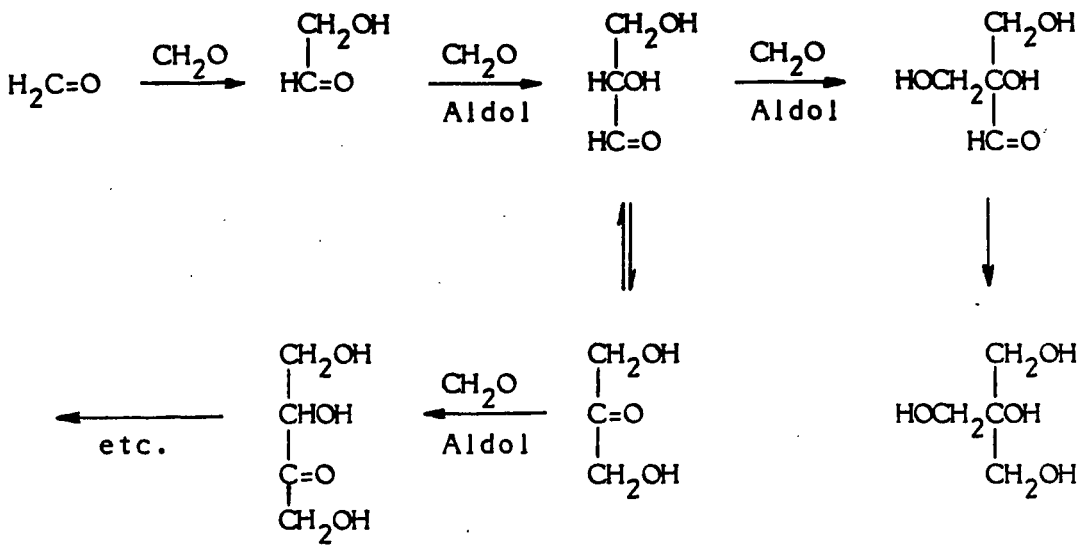


Figure 2. Proposed mechanism of the formose reaction.

with lithium dimethylamide under the carbene hydrogenation conditions gave rise to a complex mixture of products (Figure 3), one of which has been tentatively identified (by gas chromatographic analysis of the trimethylsilyl-derivatized product)[78,79] as glucose. Though Matsuura has reported a selective formose reaction,[80,81] the conditions required to achieve selectivity are quite specific and, in general, a complex formose "syrup" is expected from the reaction. Analysis of the product mixture from the $Cr(CO)_6/LiNMe_2$ hydrogenation in THF suggested that formose-type products may be present, but in no more than trace amounts (as might be expected if the relatively small amount of formaldehyde anticipated as a product of the reaction were to partition itself nonselectively among thirty to forty formose products). This is a potentially exciting observation, as the technology for

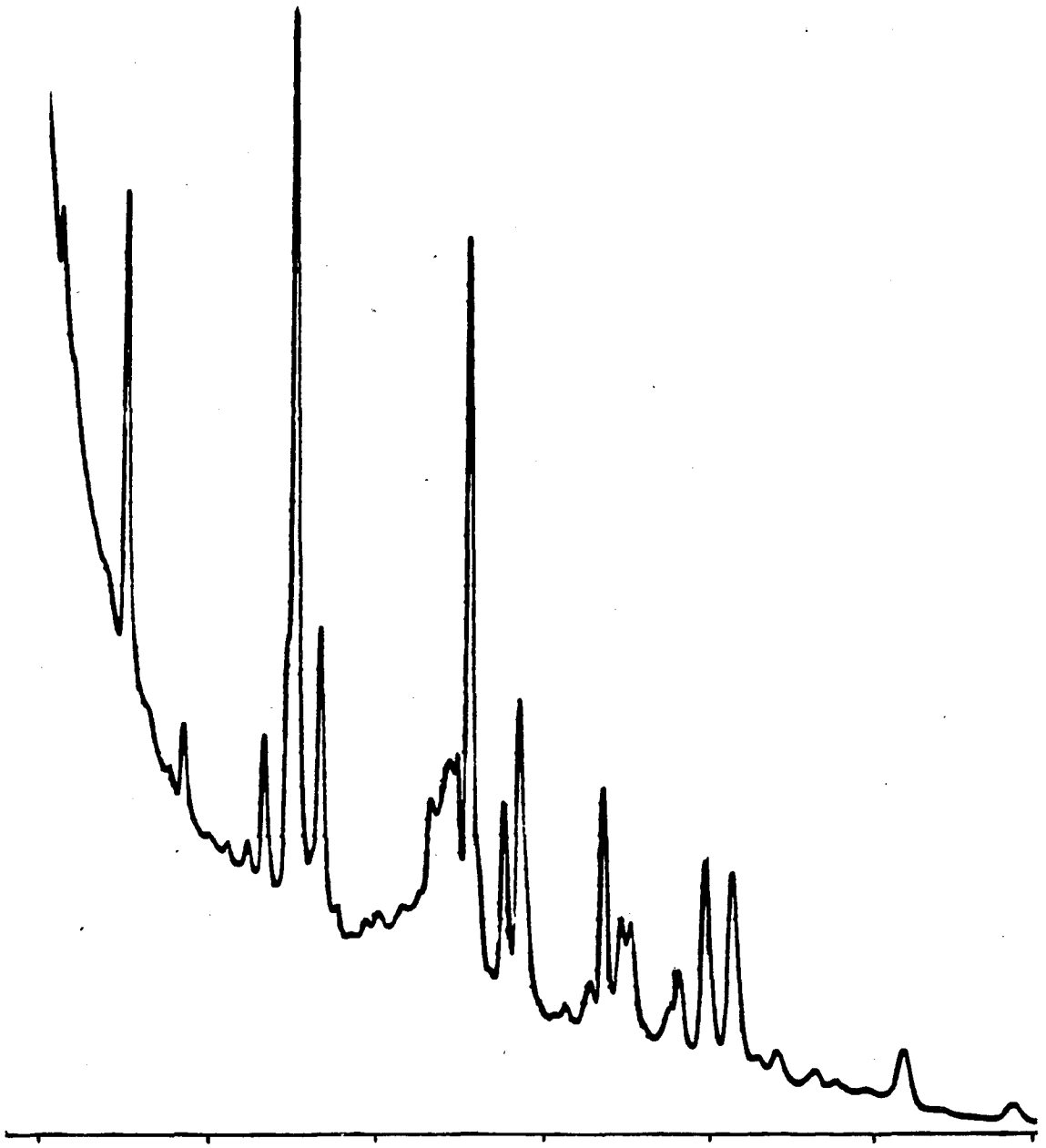
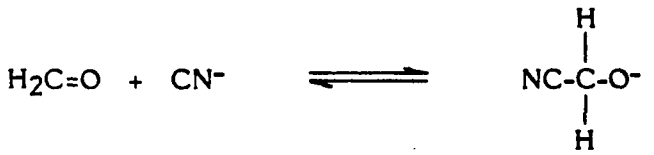


Figure 3. $LiNMe_2$-Catalyzed formose reaction.

converting formose-type products to usable molecules (e.g., ethylene glycol) is developing.[82] However, unless or until a more reliable and sensitive analytical technique is devised, any excitement must, of necessity, be modulated.

Given the plethora of reaction pathways open to formaldehyde, particularly in the presence of strong bases, if it were to be formed in the proposed catalytic system, the advantages inherent in using nucleophiles of less basicity than lithium dimethylamide become obvious. Cyanide ion appeared to be an ideal candidate, as it is a reasonably good nucleophile, but is unable to react with formaldehyde in any manner other than simple addition to the carbonyl carbon.[43]



Chromium hexacarbonyl was treated with potassium cyanide, solubilized as the crown ether complex,[83] KCN·18-crown-6, in THF and subjected to the carbene hydrogenation conditions. As with lithium dimethylamide as the activating nucleophile, a low (10%) yield of methanol was obtained. However, repetition of the experiment using carbon-13 enriched $Cr(CO)_6$ led to unenriched methanol, suggesting that the methanol was, perhaps, arising from some sort of reductive degradation of the crown ether solubilizing agent. To eliminate this source of confusion, the hydrogenation of a mixture of $W(CO)_6$ and tetrabutylammonium cyanide was examined. In this case,

however, the only reaction observed was the Hoffmann degradation of the tetrabutylammonium counter-ion, yielding 1-butene as the only characterized product. In a final attempt to avoid the problem of solubilizing agent degradation, a mixture of $Cr(CO)_6$ and a twenty-five fold excess of potassium cyanide in THF was hydrogenated. Though the system was heterogeneous initially, much of the undissolved potassium cyanide gradually dissolved as the reaction proceeded. No organic products were detected, however, and the observed rise in pressure corresponded well with the loss of three carbon monoxides per chromium, generating the known[84] $(CO)_3Cr(CN)_3^{3-}$. With no reason to expect more interesting behavior, with regards to the proposed catalysis of organic product formation from carbon monoxide and hydrogen, of other simple metal systems with cyanide ion, the reaction of $Cr(CO)_6$ with lithium dimethylamide was reinvestigated.

Reexamination of the gas chromatographic analysis of the product mixture from the hydrogenation of $Cr(CO)_6$ and lithium dimethylamide in THF revealed a sizeable peak at very long retention time. Isolation by preparative gas chromatography followed by proton NMR analysis showed the peak to be due to N,N-dimethylformamide (DMF), as was confirmed by gas chromatography/mass spectral analysis.

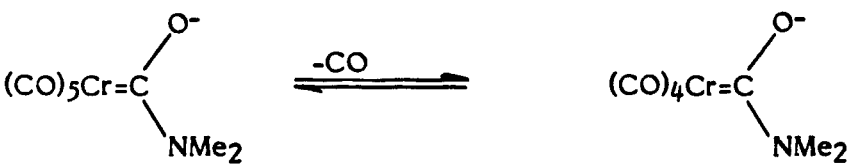
$$Cr(CO)_6 + LiNMe_2 \xrightarrow[THF]{H_2} \underset{(10\%)}{CH_3OH} + \underset{(30\%)}{HC(=O)NMe_2}$$

As solids were precipitated during the course of this hydrogenation, solvents

in which homogeneity was maintained were sought. When the hydrogenation was carried out in benzene instead of THF, the reaction mixture was heterogeneous, and no identifiable organic products were obtained. When hexamethylphosphoric triamide (HMPA) was used as the solvent, however, no solids were precipitated; the reaction mixture remained homogeneous. Though only traces of methanol were observed in this reaction (suggesting that heterogeneously catalyzed processes were indeed responsible for its formation in THF), DMF was formed, in somewhat lower yield than in THF (15%). The low yield of DMF obtained appears to be due to problems with the formation and thermal stability of the anionic carbene complex, **1**; if the reaction is run with preformed carbene complex, the DMF yield is increased to 35%, while if the reaction is run at 70°C instead of 130°C, a 40% yield of DMF is obtained (Table 3).

A reasonable mechanism for DMF formation is suggested in equations 6-9.

(6)

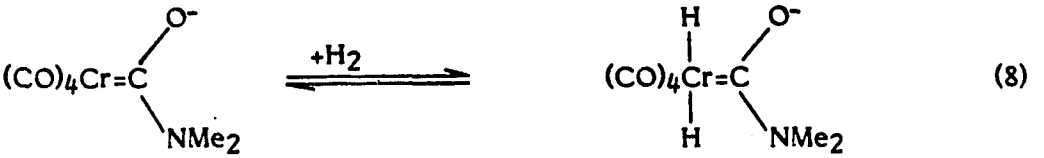


(7)

Table 3. Stoichiometric transition metal carbene complex hydrogenations.[a]

Metal Carbonyl	Solvent	Product Yields, %		
		DMF	Me_3N	Other
$Cr(CO)_6$	THF	30	--	CH_3OH (10%)
$Cr(^{13}CO)_6$	THF	[b]	--	$^{13}CH_3OH$
$Cr(CO)_6$	HMPA	15	5	--
$Cr(CO)_6$	HMPA[c]	23	3	--
$Cr(CO)_6$	HMPA[d]	[b]	--	Me_3N-d_3
$Cr(CO)_6$	HMPA[e]	40	--	--
$Cr(CO)_6$	HMPA/DMA[f]	[b]	[b]	Me_2NEt
$Cr(^{13}CO)_6$	HMPA	[b]	--	Me_3N-$^{13}C_1$
$(CO)_5Cr{=}C(OLi)NMe_2$[g]	HMPA	35	5	--
$Mo(CO)_6$	HMPA	17	trace	--
$W(CO)_6$	HMPA	18	--	--
$Mn_2(CO)_{10}$	HMPA	--	2	--
$Re_2(CO)_{10}$	HMPA	10	2	--
$Fe(CO)_5$	HMPA	8	8	--

[a]Except as noted, all reactions run with ∿3.5 mmol of metal carbonyl and an equimolar amount of $LiNMe_2$ in 5 mL of solvent under 35 psi H_2 at 130°C for 24 h. [b]Product present; yield not determined. [c]75 psi H_2. [d]35 psi D_2. [e]70°C. [f]DMA = N,N-dimethylacetamide. [g]No added $LiNMe_2$; complex synthesized by the method of Fischer, et al. (Ref. 68).



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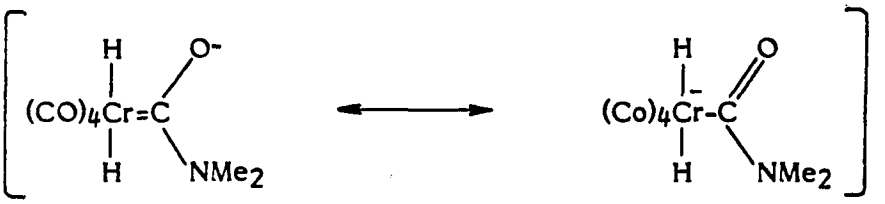

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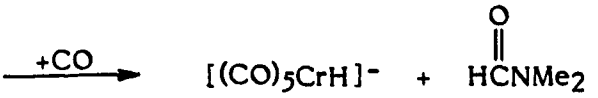
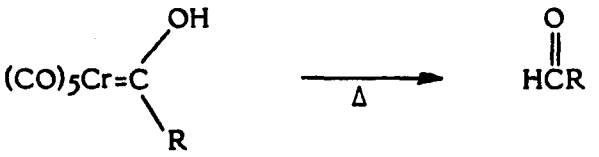
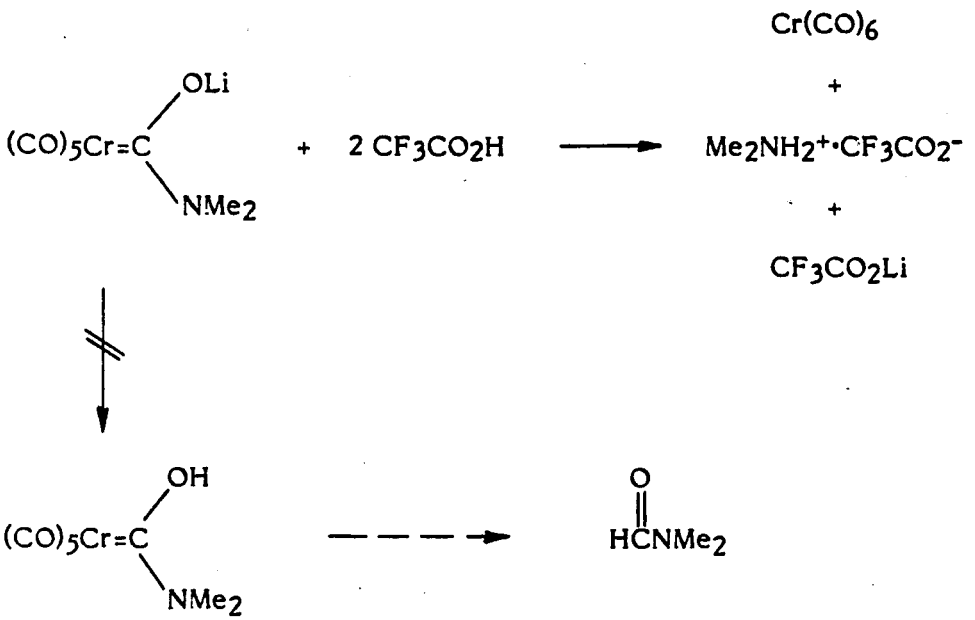


Prior carbon monoxide dissociation (eq. 7) is proposed in accord with Casey's observation[49] that temperatures in excess of that required to promote carbon monoxide dissociation are required for an appreciable rate of hydrogenation. The carbene complex is redrawn as an anionic carbamoyl complex in equation 9 to show more clearly the postulated reductive elimination step. An alternative mechanism for DMF formation involving protonation of the anionic carbene complex **1** followed by thermal decomposition to give DMF, behavior observed in alkyl substituted carbene complexes



is ruled out by the observation that treatment of the anionic complex 1 with acid results in protonation at nitrogen rather than at oxygen; no DMF is produced.



In addition to DMF, the $Cr(CO)_6/LiNMe_2$ reaction in HMPA solvent gave rise to a low (~5%) but reproducible yield of trimethylamine (Me_3N). Several significant observations with regards to its formation were made for this system. If the reaction was run under deuterium (D_2) instead of hydrogen, the Me_3N product displayed a mass spectrum consistent with Me_3N-d_3,while if carbon-13 enriched $Cr(CO)_6$ was used, the Me_3N was similarly enriched. Hydrogenation at 70°C instead of 130°C gave no Me_3N, though DMF was still formed. Finally, hydrogenation in the presence of N,N-dimethylacetamide gave rise to both Me_3N and N,N-dimethylethylamine. (In addition, a trace of ethylene contaminant in one reaction was slowly hydrogenated to ethane over the course of several days at 130°C). Apparently, then, Me_3N arises from

further reduction of the primary product, DMF. Given the mechanistic scheme proposed in equations 6-9, it seems likely that the active hydrogenation agent is the $[(CO)_5CrH]^-$ anion. Whereas the metal precipitated when the reaction was run in THF, the homogeneity of the HMPA solutions suggests the metal fragment is stabilized in solution, most likely by replacement of some carbon monoxide ligands by HMPA. In fact, gas evolution was observed at the start of the reactions in HMPA -- though the identity of the gas is unknown, it is very likely carbon monoxide (which is not detected on gas chromatographs equipped with flame ionization detectors). An infrared spectrum of a solution of $Cr(CO)_6$ and lithium dimethylamide in HMPA, after heating under argon until gas evolution ceased, showed a multitude of νCO bands in the metal carbonyl region, suggesting that a complex mixture of $[Cr(CO)_n(HMPA)_{5-n}(CONR_2)]^-$ species was indeed present.[85]

The $[(CO)_5CrH]^-$ anion was independently prepared as the tetraethylammonium salt as reported by Darensbourg,[87] and a solution of DMF in HMPA was treated with this hydride under the carbene hydrogenation conditions. Unfortunately, Hoffmann degradation of the counter-ion produced triethylamine and ethylene (both observed by gas chromatography), and in the process must also have liberated a proton, which presumably reacted with $[(CO)_5CrH]^-$ to produce hydrogen.

$$Et_4N^+ [(CO)_5CrH]^- \xrightarrow[\Delta]{} Et_3N + H_2C{=}CH_2 + H_2 + [Cr(CO)_5]$$

No products derived from the reduction of DMF were observed. If, however, the thermally stable bis(triphenylphosphine)iminium (PPN^+) salt of the $[(CO)_5CrH]^-$

anion was used, quantitative (based on chromium complex) reduction of DMF to Me_3N was observed.[88] Similar results were obtained for N,N-dimethylacetamide and N,N-diethylacetamide; the corresponding amines (N,N-dimethylethylamine and triethylamine, respectively) were obtained in at least quantitative yield. (Dimethylsulfoxide is an equally effective solvent for these reductions). Though yields in most cases appeared to be greater than quantitative, they are not sufficiently greater to firmly demonstrate catalytic functioning of the chromium hydride anion. Nevertheless, these are exceptionally mild conditions (130°C, 35 psi H_2) for a transition metal mediated reduction of an amide to an amine (typical conditions using heterogeneous copper chromite catalysts[90] are 300°C, 300 atm H_2) and in fact there are no other known examples of the homogeneous reduction of amides by transition metal complexes. It is interesting that a soluble organometallic system specifically designed as a potent hydride reducing agent,[91] while capable of reducing esters to alcohols,[91] is completely inert toward amide reduction.[92]

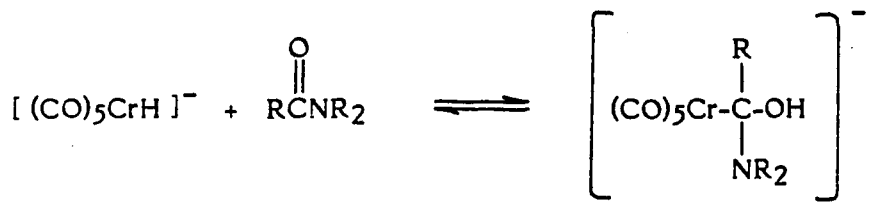
$$(PPh_3)(PPh_2)RuH_2^-K^+\cdot(diglyme)_2 + CH_3CO_2CH_3 \xrightarrow[90°C]{H_2} \begin{matrix} CH_3OH \\ + \\ CH_3CH_2OH \end{matrix}$$

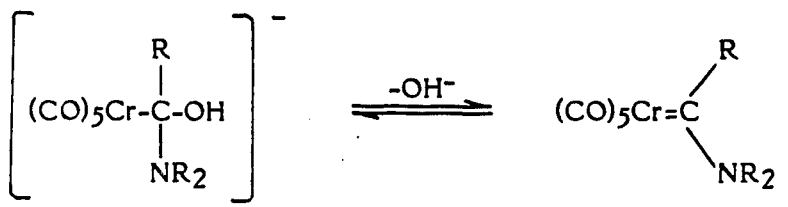
$$\downarrow \quad RC(=O)NR_2$$

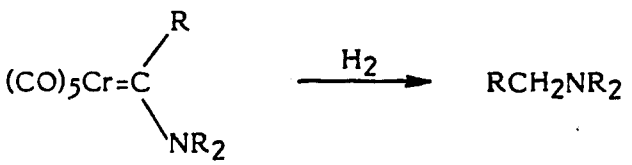
no reaction

The $[(CO)_5CrH]^-$ anion appears to be the antithesis of this ruthenium hydride, in that it bears strongly electron-withdrawing carbonyl ligands

rather than donating phosphine ligands, yet it displays unprecedented reducing activity. This observation may possibly be a consequence of a key mechanistic difference between the two reducing systems; whereas the ruthenium hydride system most certainly reacts as a hydride donor, perhaps the $[(CO)_5CrH]^-$ anion accomplishes amide reduction via carbonyl oxygen protonation, as suggested below.







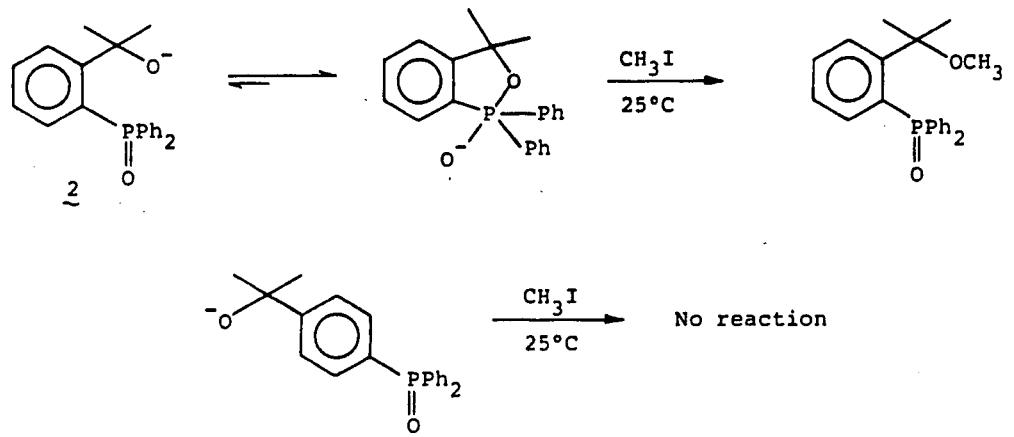
Use of a series of binary transition metal carbonyl complexes in place of $Cr(CO)_6$ in the lithium dimethylamide/HMPA reductions has been investigated; the results are summarized in Table 3. Though most of the metals studied generated DMF, only $Fe(CO)_5$ gave Me_3N yields comparable to those found for $Cr(CO)_6$. Dicobalt octacarbonyl also generated DMF and Me_3N, but is not listed in Table 3, as the reaction mixture did not remain

homogeneous --cobalt metal was precipitated; in addition, tetramethylurea was produced in a vigorous exothermic reaction before hydrogenation. Finally, the group 6B metals ($Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$) appeared to produce small amounts of lower hydrocarbons (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, 1-C_4H_8, n-C_4H_{10}) upon acidolysis of aliquots of the reaction mixtures. Yields were extremely low, however (typically 0.1-1.0% based on metal carbonyl), precluding the labeling studies essential to a critical evaluation of these observations.

Though homogeneous systems have been found which are able to reduce transition metal bound carbon monoxide to a formyl group (in DMF) and a methyl group (in Me_3N) once it is activated by nucleophilic attack,[93] the activating nucleophile is incorporated in the products observed. Weaker nucleophiles seem desirable, in that they may be more prone to facile release from organic intermediates formed, thus allowing recycling of nucleophiles in a catalytic sequence. However, as discussed above, weaker nucleophiles, such as alkoxides or cyanide ion, show little tendency to react with neutral transition metal carbonyls. Species of intermediate nucleophilicity are fortunately available, and the reactions of $Cr(CO)_6$ with two of these, lithium methylphenylamide (LiNMePh) and lithium diphenylamide ($LiNPh_2$) were investigated. Treatment of $Cr(CO)_6$ with LiNMePh afforded good yields of spectroscopically pure $(CO)_5Cr{=}C(OLi)(NMePh)$, and hydrogenation of this carbene complex under the usual conditions (35 psi H_2, 130°C, HMPA solvent) generated a moderate yield of methanol ($\sim$10%). No products analogous to those obtained from $LiNMe_2$, i.e., the corresponding formamide (HC(O)NMePh) or methylated amine ($PhNMe_2$) were detected; the sole nitrogeneous

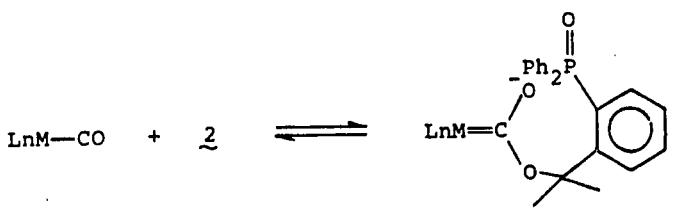
compound isolated proved to be simply the parent amine, N-methylaniline (PhNHMe). Hydrogenation of a 1:1 mixture of $Cr(CO)_6$ and LiNMePh, rather than of the isolated carbene complex, unfortunately afforded only N-methylaniline; no methanol was produced. Attempts to prepare pure samples of $(CO)_5Cr{=}C(OLi)(NPh_2)$ were unsuccessful; apparently the equilibrium for nucleophilic attack by $LiNPh_2$ is such that nearly equal amounts of reactants and products are present, and isolation attempts led only to mixtures of $LiNPh_2$ and the desired carbene complex. ($Cr(CO)_6$ is volatile and was removed upon workup.) Hydrogenation of a 1:1 mixture of $Cr(CO)_6$ and $LiNPh_2$, as in the case of LiNMePh, generated only the amine, diphenylamine; no carbon monoxide-derived organic products were detected.

Though enhanced carbon monoxide reduction to organic products not containing the activating nucleophile has been obtained (with the preformed carbene complex $(CO)_5Cr{=}C(OLi)(NMePh)$), the observation of simple protonation of weaker nucleophiles in the presence of $Cr(CO)_6$ and hydrogen is disturbing; this complication will be discussed in greater detail in Chapter II. Apparently, more elegant systems will be required to induce weaker nucleophiles to attack transition metal bound carbon monoxide. One such system was suggested by a recent report of an organic alkoxide of extraordinary nucleophilicity.[94] The ortho-diphenylphosphinyl derivative, 2, which in solution at room temperature is predominantly in the form of the anionic cyclic oxyphosphorane, reacts with methyl iodide at room temperature to give the corresponding methyl ether, whereas the para isomer does not react with methyl iodide under similar conditions.

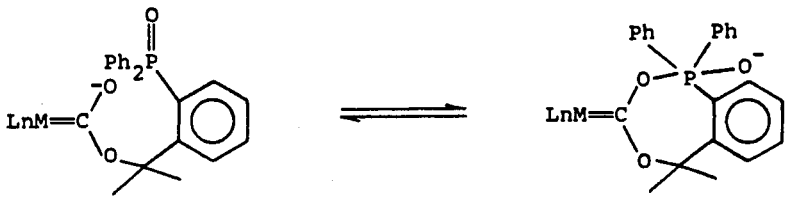


The enhanced nucleophilicity of the ortho isomer **2** is ascribed to a weakening of the alkoxide-counter-ion (Na^+) interaction by the adjacent phosphine oxide, giving rise to a "barer", more reactive alkoxide.

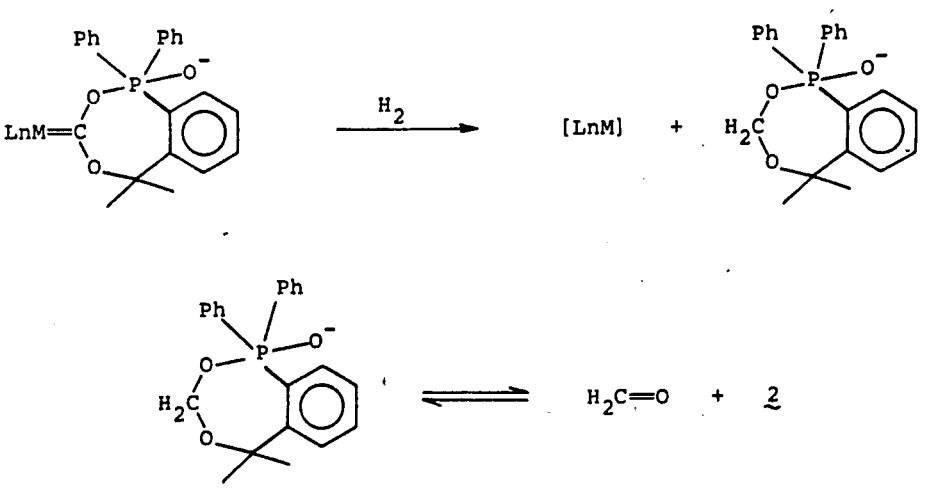
The reactive alkoxide **2** should be capable of nucleophilic attack at transition metal bound carbon monoxide.



Even if this initial attack is somewhat unfavorable (as observed previously for simple alkoxides), cyclization to the cyclic oxyphosphorane should drive the equilibrium.



In addition, this cyclization forces the complex into a carbene-like form, thereby potentially facilitating the transfer of two hydrogens to carbene carbon upon hydrogenation (whereas only one hydrogen is transferred in complex **1**, which electronically behaves more as an anionic carbamoyl complex, as suggested in equation 9, than as a carbene complex) and making possible the catalytic functioning of the nucleophile **2**.[95]



The synthesis[98] of alkoxide **2** is outlined in Figure 4. Treatment of **2** with $(CpFe(CO)_3)^+PF_6^-$, a complex[99,100] known to be susceptible to nucleophilic attack by alkoxides,[100] afforded the desired adduct; however,

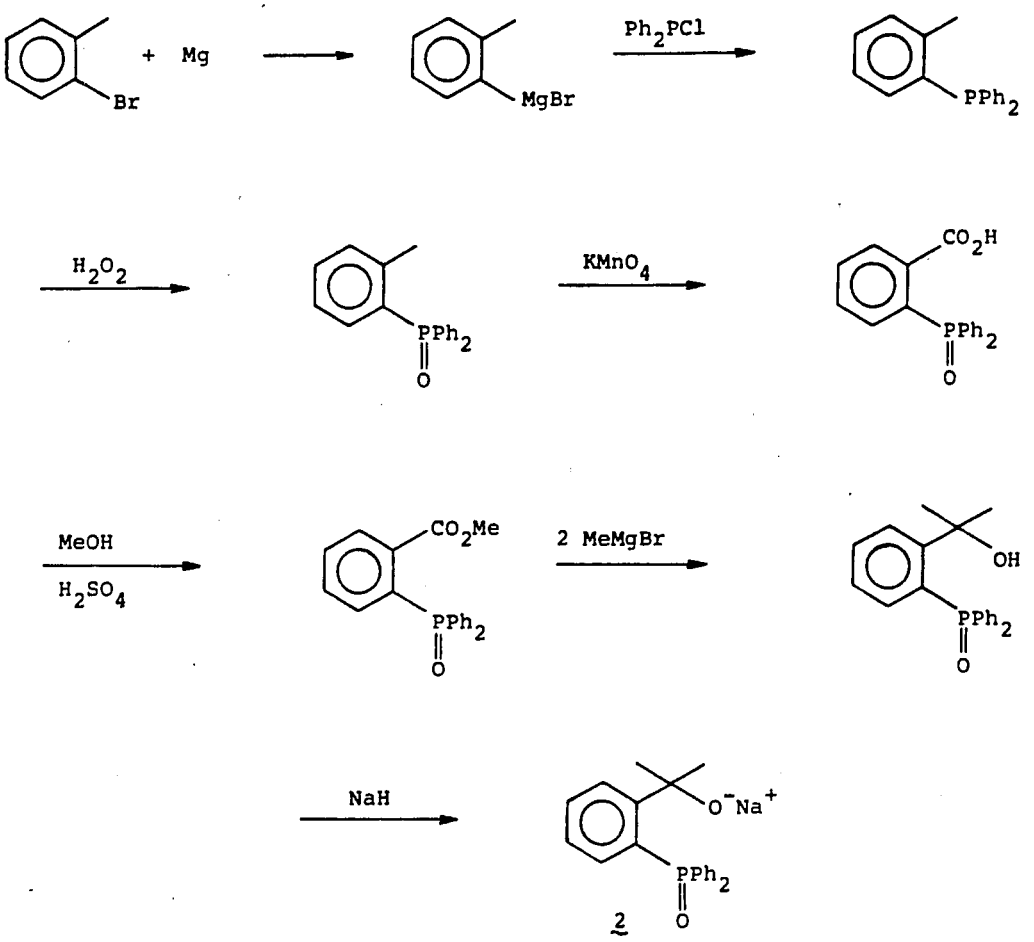
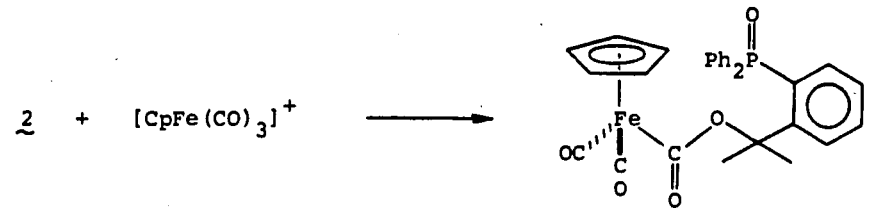
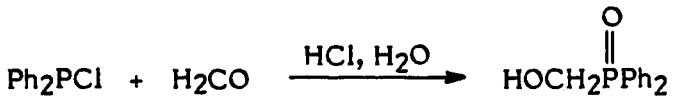


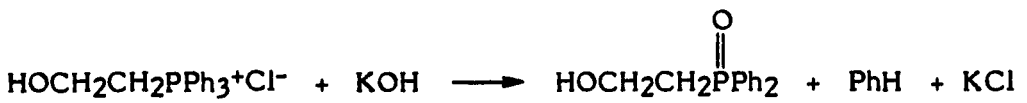
Figure 4. Synthesis of an alkoxide of extraordinary reactivity.



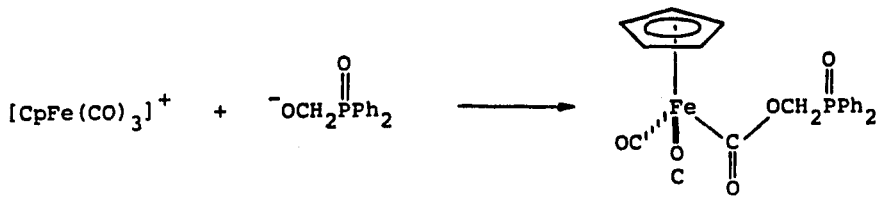
the infrared spectrum of this adduct displayed a C=O stretch at 1645 cm^{-1}, indicative of a simple metalloester.[100] As seven-membered rings are not highly favored in cyclic oxyphosphoranes,[101] systems related to alkoxide **2** which would give rise to energetically more favorable five- and six-membered rings were explored. Hydroxymethyldiphenylphosphine oxide is readily produced in multi-gram quantities in a one-step reaction.[102]



The hydroxyethyl derivative, also reported in the literature,[103] is more difficult to prepare, though gram quantities of it are also available.

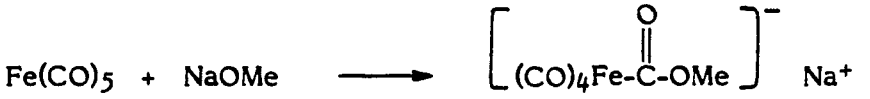


Deprotonation of these hydroxyalkyl species with sodium hydride appears to proceed cleanly; loss of the diphenylphosphinyl anion is not observed in these deprotonated species. The alkoxide derived from hydroxymethyldiphenylphosphine

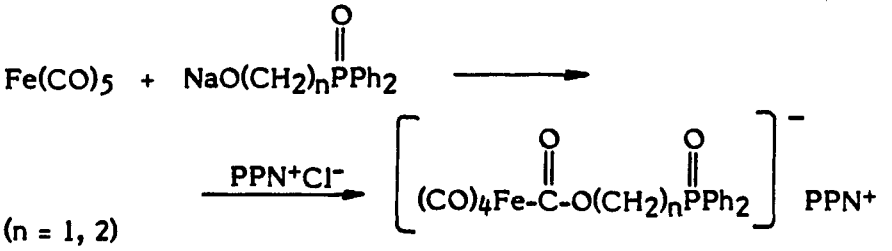


oxide reacts readily with $(CpFe(CO)_3)^+PF_6^-$; again, however, infrared evidence demonstrates the lack of cyclization in this system. This observation is confirmed by the ^{31}P NMR spectrum of the product; no resonance is observed in the region between 0 and -40 ppm (vs 85% H_3PO_4) expected for such an anionic oxyphosphorane.[94,101]

Iron pentacarbonyl is well-known to react with carbon nucleophiles;[104,105] reactions with alkoxides are, however, unreported. Sodium methoxide reacts readily with $Fe(CO)_5$, giving an orange, crystalline, rather unstable product which appears on the basis of ^1H NMR and infrared spectroscopic evidence to be the metalloester.

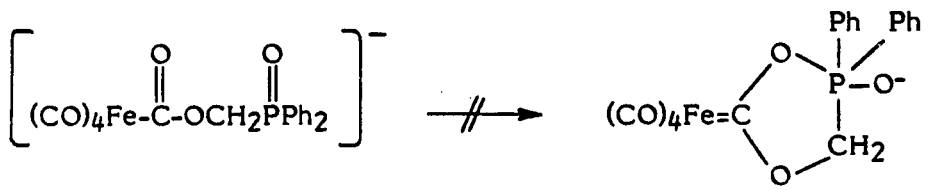


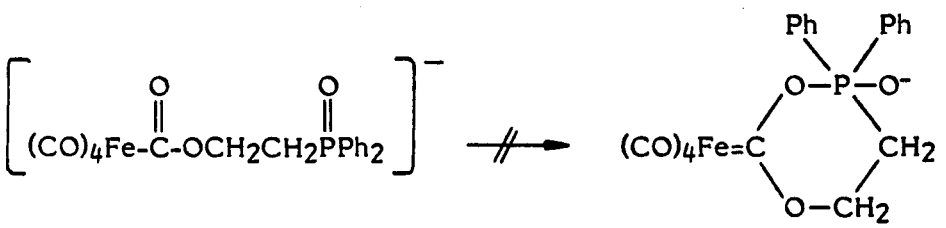
The phosphine oxide alkoxides also react with $Fe(CO)_5$, giving orange-red solids after counter-ion exchange (attempted isolation as the Na^+ salt resulted in rapid decomposition).



(n = 1, 2)

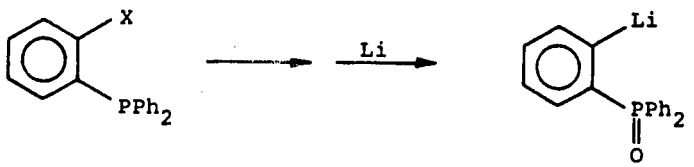
Both complexes display ^{31}P NMR and infrared spectra consistent with the open-chain metalloester forms; no cyclization to the oxyphosphorane form is evident.





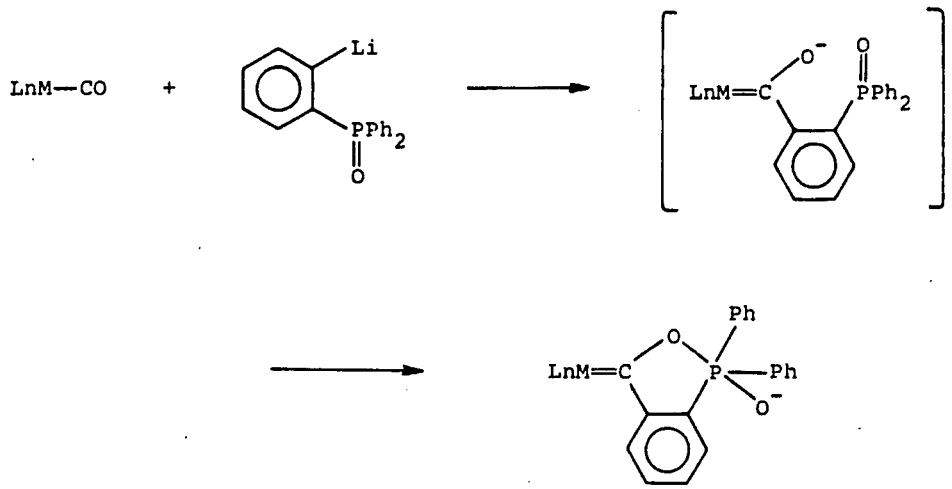
Attempted recrystallization to obtain samples for elemental analysis resulted in decomposition; deep red crystals were obtained, but this unidentified complex no longer displayed ^{1}H NMR signals assignable to the alkoxide functionality.

Thus, it would appear that these functionalized phosphine oxide systems will be incapable of providing the desired activation of transition metal bound carbon monoxide. A related system that should indeed give rise to a cyclic oxyphosphorane complex is ortho-diphenylphosphinylphenyllithium which, though unknown, should be obtainable from the known ortho-halo phosphines.[106]



X = Br, Cl

This lithium reagent should react with transition metal bound carbon monoxide, and the products of such reactions will almost certainly be in the cyclized form.



This nucleophile, of course, will not function catalytically, as the carbon-carbon bond formed is not likely to be broken under ordinary conditions.

Summary

Intermolecular attack at transition metal bound carbon monoxide by very strong nucleophiles ($LiNMe_2$) activates carbon monoxide for reduction by molecular hydrogen. The products of this reduction incorporate the

activating nucleophile, precluding the catalytic function desired. Weaker nucleophiles (LiNMePh, $LiNPh_2$) show some promise for formation of products not incorporating the nucleophile; however, these systems also point out a possible problem related to the use of weaker nucleophiles -- nucleophile protonation becomes competitive (LiNMePh) or dominant ($LiNPh_2$) over nucleophilic attack at transition metal bound carbon monoxide. A series of functionalized phosphine oxide species designed to overcome this problem has been examined; in no case is the desired carbene complex formation observed.

Experimental Section

All organometallic reactions were carried out using standard inert atmosphere techniques. Complexes were stored in a Vacuum Atmospheres inert atmosphere (N_2) drybox equipped with an MO-40 Dri-Train. Metal carbonyls [$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Co_2(CO)_8$] were purchased from Pressure Chemical Co. (Pittsburgh, PA) and used as received. Lithium dimethylamide and $Fe(CO)_5$ were obtained from Alfa Products (Thiokol/Ventron Division), carbon-13 enriched carbon monoxide from Monsanto-Mound Laboratories, and tetrabutylammonium cyanide from Tridom-Fluka. Other reagents were obtained from standard commercial sources.

Tetrahydrofuran (THF), benzene, pentane, and hexane were dried and deoxygenated over sodium/benzophenone ketyl, solubilized with tetraglyme in all except THF. Acetonitrile and dichloromethane were dried over CaH_2 and degassed in vacuo. Methanol was dried over Linde 4A molecular sieves and degassed in vacuo. All solvents were stored under argon, generally in solvent storage flasks equipped with Teflon valves. Hexamethylphosphoric triamide (HMPA) was stirred over CaH_2, then vacuum distilled onto sodium metal. After the solution became deep blue, HMPA was vacuum distilled, then stored over Linde 4A molecular sieves in the inert atmosphere box.

Carbon-13 enriched $Cr(CO)_6$ was prepared by heating $Cr(CO)_6$ in THF under 35 psi ^{13}CO at 130°C for four days, then filtering off the crystalline material which precipitated upon cooling. The anionic carbene complex,[68] $(CO)_5Cr{=}C(OLi)(NMe_2)$ (1), KCN·18-crown-6,[83] alkoxide 2,[94,98] $[CpFe(CO)_3]^+PF_6^-$,[99,100] hydroxymethyldiphenylphosphine oxide,[102]

hydroxyethyldiphenylphosphine oxide,[103] and disodium pentacarbonylchromate, $Na_2Cr(CO)_5$[107] were all prepared as described.

General Hydrogenation Procedure. Hydrogenations were carried out in a glass pressure vessel equipped with a metal pressure head bearing a pressure gauge, a gas inlet valve, a safety valve set to release at 100 psi, and a ball valve fitted with a gas chromatography injection port septum for gas sampling. The pressure vessel was charged with solid reactants and solvent in the inert atmosphere box. After sealing to the pressure head (Neoprene O-ring seal), the apparatus was removed from the box, connected to a hydrogen line, and repeatedly pressured to 35 psi H_2 and vented. Finally, the system was brought to 35 psi H_2, all valves were sealed, and the lower part of the apparatus was immersed in a silicone oil bath at the desired temperature (usually 130°C). Vapors were periodically sampled by gas-tight syringe; solutions were analyzed after cooling and venting excess pressure. Reactions were typically terminated after 24 h. Vapors and solutions were analyzed for volatile products derived from carbon monoxide reduction by gas chromatography on a 9-ft Porapak Q column, programmed from 110°C to 175°C at 4°/min, N_2 carrier, 35 mL/min flow rate, injector and detector temperatures 200°C, flame ionization detector. Solutions were further analyzed, both before and after trimethylsilylation by the method of Sweeley, et al.,[79] on a 12-ft 3% SE-30 on Chromosorb Q column, programmed from 65°C to 230°C at 6°/min, N_2 carrier, 10 mL/min flow rate, injector and detector temperatures 200°C, flame ionization detector, or on a 12-ft 3% SE-52 column under the same conditions. Analysis for lower aliphatic amines was carried out on a 6-ft Carbopack B/4% Carbowax 20 M/0.8% KOH column

at 70°C, N_2 carrier, flow rate 20 mL/min, other conditions as above, and on other columns as noted below. Other gas chromatographic analyses, used in special cases, are also detailed below.

$(CO)_5W{=}C(OLi)(CH_3)$. The anionic tungsten carbene complex (1.0 g), prepared as described,[50] was dissolved in 20 mL of THF and hydrogenated at 130°C. After 16 h, the solution was sampled and acidified. Gas chromatography (GC) on a 32-ft Carbowax 600 column at 100°C demonstrated the presence of ethanol, formed in greater than 50% yield (by GC-external standard technique[108]).

$(CO)_5Cr{=}C(OLi)(NMe_2)$. (a) THF. The anionic chromium carbene complex, **1**, was prepared as described.[68] The hydrogenation of 1.5 g of **1** in 15 mL of THF was carried out at 130°C for 48 h. GC analysis of the solution on Porapak Q showed the presence of either formaldehyde or methanol (inseparable on Porapak Q). Repetition of the hydrogenation using carbon-13 enriched **1** (prepared from enriched $Cr(CO)_6$), followed by GC/mass spectral (GC/MS) analysis on Porapak Q, showed the product to be methanol (carbon-13 enriched); yield was roughly 10% (by GC-external standard technique). Similar results were obtained when equimolar amounts of $Cr(CO)_6$ (1.5 g, 6.8 mmol) and $LiNMe_2$ (0.35 g, 6.8 mmol) were dissolved in 10 mL of THF and subjected to hydrogenation. In addition, N,N-dimethylformamide (DMF) was obtained from this reaction in ~30% yield (by GC-standard addition technique). Confirmation of DMF production was obtained by GC/MS on Porapak Q and by ^1H NMR of isolated product from preparative scale gas chromatographic separation of the mixture; DMF yield was quantified using a 10-ft 10% Versamid 900 on Chromosorb Q column at 70°C, N_2 carrier, 40

mL/min flow rate.

(b) C_6H_6. Hydrogenation of 1.5 g $Cr(CO)_6$ (6.8 mmol) and 0.35 g $LiNMe_2$ (6.8 mmol) in 10 mL of benzene at 130°C yielded a heterogeneous brown mixture. No characterizable products were detected by GC on Porapak Q.

(c) HMPA. Hydrogenation of 1.5 g $Cr(CO)_6$ (6.8 mmol) and 0.35 g $LiNMe_2$ (6.8 mmol) in 10 mL of HMPA at 130°C yielded a homogeneous yellow solution. GC of the vapor phase on Porapak Q showed the presence of Me_3N, confirmed by GC/MS on Porapak Q. The same reaction under deuterium gas (D_2) led to Me_3N product which, as demonstrated by GC/MS, contained three deuterium atoms per molecule. The reaction under hydrogen at 70°C gave only traces of Me_3N, but DMF was detected in solution. Finally, repetition of the hydrogenation at 130°C in the presence of excess N,N-dimethylacetamide (2 mL) yielded Me_3N and N,N-dimethylethylamine ($EtNMe_2$) in the vapor phase. (Production of $EtNMe_2$ was confirmed by comparison of retention time with authentic $EtNMe_2$, prepared by $LiAlH_4$ reduction of N,N-dimethylacetamide and purified as the hydrochloride.)

$Cr(CO)_6$ + KCN·18-Crown-6. Hydrogenation of a mixture of 0.5 g $Cr(CO)_6$ (2.27 mmol) and 0.748 g KCN·18-crown-6[83] (2.27 mmol) in 10 mL of THF at 130°C for 24 h gave rise to methanol (~10% yield). Repetition using carbon-13 enriched $Cr(CO)_6$ led to unenriched methanol (by GC/MS).

$Cr(CO)_6$ + KCN. A mixture of 0.5 g $Cr(CO)_6$ (2.27 mmol) and 0.148 g KCN (2.27 mmol) in 10 mL THF, hydrogenated at 130°C for 24 h, gave no detectable organic products. Use of a 25-fold excess of KCN (3.7 g, 56.8 mmol) led to a pressure increase corresponding to loss of three carbon

monoxides per chromium; no organic products were found.

$W(CO)_6$ + $^nBu_4N^+CN^-$. Hydrogenation of 0.5 g $W(CO)_6$ (1.42 mmol) and 0.381 g $^nBu_4N^+CN^-$ (1.42 mmol) in 10 mL THF at 130°C for 24 h yielded 1-butene (GC on Porapak Q) but no other identified organic products.

Metal Carbonyls + $LiNMe_2$. The following procedure was used for $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe(CO)_5$, and $Co_2(CO)_8$. A pressure bottle was charged with equimolar amounts (~3.5 mmol) of the metal carbonyl and $LiNMe_2$ in the drybox ($Fe(CO)_5$ was added outside the drybox through the septum-capped ball valve). HMPA (5 mL) was added, the bottle was sealed to a pressure head, and the apparatus was removed from the drybox. Hydrogenation as above was followed by GC analysis on Porapak Q (for volatile products) and on the Versamid 900 column (for DMF and tetramethylurea). Results are summarized in Table 3.

Infrared Analysis of $Cr(CO)_6$ + $LiNMe_2$ + HMPA Reaction. Chromium hexacarbonyl (0.75 g, 3.4 mmol) and $LiNMe_2$ (0.175 g, 3.4 mmol) were dissolved in 5 mL HMPA in a glass pressure bottle. The bottle was pressured to 35 psi with argon. Heating at 130°C resulted in apparent gas evolution (bubbling), which ceased after ~10 min, and a dark orange-red solution. The mixture was cooled to room temperature; the pressure had risen to 40 psi. An aliquot of the solution was withdrawn and diluted with HMPA under argon. The infrared spectrum of this solution showed multiple metal carbonyl stretching bands, at 1940, 1913, 1903, 1885, and 1857 cm^{-1}, whereas $Cr(CO)_6$ shows a single stretch at 1985 cm^{-1} and $(CO)_5Cr{=}C(OMe)Me$ has stretches at 2068, 1966, and 1949 cm^{-1}.

Protonation of $(CO)_5Cr{=}C(OLi)(NMe_2)$ (1). A sample of complex 1 was

dissolved in dry acetone-d_6 in an NMR tube in the inert atmosphere box. The ^1H NMR spectrum of 1 consists of a broad singlet at δ 2.28,plus peaks due to a THF solvate molecule. Excess CF_3CO_2H was added via syringe, causing a crystalline white solid ($Cr(CO)_6$) to precipitate. The broad singlet in the ^1H NMR shifted to δ 2.78, a region characteristic of N-protonated amines (i.e., $Me_2NH_2^+$). Heating at 130°C for 5 min gave no change. To the limits of NMR detection, no DMF was formed.

$LiNMe_2$-Catalyzed Formose Reaction. A suspension of 1.5 g paraformaldehyde (50 mmol) and 0.35 g $LiNMe_2$ (6.9 mmol) in 20 mL THF was heated at 130°C under 35 psi H_2 for 24 h. GC of the vapor phase on Porapak Q showed mainly formaldehyde. When the solution was trimethylsilylated[79] (0.1 mL solution was treated successively with 0.5 mL pyridine, 0.1 mL hexamethyldisilazane, and 0.05 mL trimethylsilyl chloride, then shaken and allowed to stand for 5 min) and examined on the SE-52 column, a multitude of peaks was obtained. Standard injections suggested the possible presence of glyceraldehyde and glucose.

Preparation of $Et_4N^+[(CO)_5CrH]^-$.[87] Acetonitrile (40 mL) was vacuum transferred onto 2.45 g $Na_2Cr(CO)_5 \cdot x\ THF$[107] in a 100 mL side-arm round-bottom flask. After warming to room temperature, the orange solution was treated with 1.5 mL MeOH, immediately forming a white precipitate. The suspension was stirred for a few minutes, then filtered through a pad of Celite, washing with THF. A solution of 3.7 g $Et_4N^+Br^-$ (dried in vacuo) in 10 mL MeOH was syringed into the filtrate, giving a deeper yellow solution and a white solid. Solvent was removed in vacuo, 30 mL THF was added, and the suspension was filtered through Celite. This process was repeated once more,

then solvent was removed in vacuo, yielding a yellow powder (1.26 g): ^{1}H NMR (CD_3CN) δ -7.0 (s, 1H, CrH), 1.2 (m, 12H, CH_3CH_2N), 3.1 (q, 8H, CH_3CH_2N); IR (THF) ν_{CO} = 2020 (w), 1885 (s), 1865 (s) cm^{-1}.

Attempted Reduction of DMF by $Et_4^+[(CO)_5CrH]^-$. In the inert atmosphere box, a pressure bottle was charged with 0.25 g $Et_4N^+[(CO)_5CrH]^-$ (0.77 mmol), 5 mL HMPA, and 0.25 mL DMF (1.36 mmol, dried over BaO and degassed in vacuo). Hydrogenation under 35 psi H_2 at 130°C resulted in the rapid formation of C_2H_4 and Et_3N (GC on SE-30). No amine products other than Et_3N were observed after 24 h.

Preparation of $PPN^+[(CO)_5CrH]^-$. This complex was prepared as described above, substituting bis(triphenylphosphine)iminium chloride (PPN^+Cl^-, 10.1 g, 17.6 mmol) for $Et_4N^+Br^-$. Trituration of the final product with hexane, followed by drying in vacuo, afforded an orange-brown powder (4.31 g): ^{1}H NMR (acetone-d_6) δ -6.7 (s, 1H, CrH), 7.7 (m, 30H, PPN^+).

$PPN^+[(CO)_5CrH]^-$ Reductions of Amides. In the inert atmosphere box, a pressure bottle was charged with 0.75 g $PPN^+[(CO)_5CrH]^-$ (1.02 mmol), 5 mL HMPA, and 1 mL of a liquid carboxylic amide (dried over BaO, degassed in vacuo). Hydrogenation under 35 psi H_2 at 130°C for 72 h was followed by gas chromatographic analysis for amine products. Details are outlined below.

(a) DMF. GC analysis on 3% SE-30, 70°C; quantification by standard addition technique, judging peak area increase upon addition of known amounts of Me_3N; yield of Me_3N ~130%, based on $[(CO)_5CrH]^-$.

(b) N,N-Dimethylacetamide. GC analysis on 3% SE-30, 70°C; quantification by internal standard technique, using methylcyclohexane as

the internal standard, yield of Me_2NEt ~120%.

(c) **N,N-Diethylacetamide.** GC analysis on 17-ft Durapak, 60°C; quantification by standard addition technique, judging peak area increase upon addition of known amounts of Et_3N; yield of Et_3N ~150%. Similar results were obtained in DMSO as solvent.

Preparation of Lithium Methylphenylamide, LiNMePh. A 250 mL side-arm round-bottom flask was flushed with argon and charged with 5.0 g N-methylaniline (0.047 mol) and 100 mL dry hexane. The flask was fitted with an argon-flushed, septum-stoppered dropping funnel charged with 29.2 mL n-butyllithium solution in hexane (1.6 M, 0.047 mol). With the flask open to a mercury bubbler and with good stirring, the butyllithium was slowly added, giving a milky white suspension. Stirring was continued for 30 min, then the mixture was filtered, under argon, on a medium fritted glass funnel. The solid was washed well with hexane, then dried in vacuo, giving a pyrophoric white powder (4.9 g, 93%) which was stored in the inert atmosphere box.

Preparation of Lithium Diphenylamide, $LiNPh_2$. This compound was prepared as described for LiNMePh, substituting 8.0 g diphenylamine (0.047 mol) for N-methylaniline. Yield 7.62 g (92%); stored in the inert atmosphere box.

Preparation of $(CO)_5Cr{=}C(OLi)(NMePh)$. In the inert atmosphere box, a 300 mL three-neck round-bottom flask was charged with 4.0 g $Cr(CO)_6$ (0.018 mol) and fitted with a stopper, a stopcock, and a solid addition arm containing 2.0 g LiNMePh (0.018 mol). The apparatus was connected to an argon line through the stopcock, and 75 mL dry THF was added. The stirred suspension of $Cr(CO)_6$ was cooled in an ice bath, and the LiNMePh was

gradually added over a period of 90 min; the solution first turned yellow, then darkened to orange-red. Residual LiNMePh was washed in with an additional 10 mL THF. After stirring at 0°C for 45 min, the solution was reduced in volume to ~15 mL in vacuo, then filtered under argon through a medium frit; the white precipitate was washed with 5 mL THF. Removal of solvent from the filtrate in vacuo afforded a pale brown powder, 6.32 g (88%). Attempted recrystallization from THF/hexane gave an oil. The ^1H NMR spectrum of the product demonstrates it to be a mono-THF solvate: ^1H NMR (acetone-d_6) δ 2.8 (s, 3H, NCH_3), 6.4-7.2 (m, 5H, NC_6H_5), 1.7 (m, 4H, THF), 3.6 (m, 4H, THF).

Attempted Preparation of $(CO)_5Cr=C(OLi)(NPh_2)$. The procedure described above for the LiNMePh reaction was followed, substituting 3.18 g $LiNPh_2$ (0.018 mol) for LiNMePh. Workup afforded 4.2 g of a brown solid. The ^1H NMR spectrum in acetone-d_6 integrates very poorly for the anticipated mono-THF solvate (~0.5 THF/Li), and this, combined with the low yield (suggesting, given the method of preparation, that much $Cr(CO)_6$ was removed in vacuo) suggests the product is a mixture of the desired carbene complex and unreacted $LiNPh_2$.

Hydrogenation of $(CO)_5Cr=C(OLi)(NMePh)$. Hydrogenation of 1.4 g (3.45 mmol) of the carbene complex was carried out under 35 psi H_2 at 130°C in 5 mL HMPA for 24 h. GC analysis of the solution on Porapak Q demonstrated the presence of methanol, formed in 10% yield (2-methylbutane internal standard). Analysis on a 6-ft Carbowax 20 M column, programmed from 150°C to 220°C at 8°/min, showed a high yield of N-methylaniline; no N-methylformanilide (HC(O)NMePh) or N,N-dimethylaniline was detected.

$Cr(CO)_6$ + LiNMePh. Hydrogenation of a mixture of 0.75 g $Cr(CO)_6$ (3.4 mmol) and 0.385 g LiNMePh (3.4 mmol) in 5 mL HMPA yielded only N-methylaniline (GC analysis on Carbowax 20 M, as above).

$Cr(CO)_6$ + $LiNPh_2$. Hydrogenation of a mixture of 0.75 g $Cr(CO)_6$ (3.4 mmol) and 0.597 g $LiNPh_2$ (3.4 mmol) in 5 mL HMPA yielded only diphenylamine (GC analysis on Carbowax 20 M, as above).

Preparation of $Cp(CO)_2FeCO_2C(Me)_2(o\text{-}C_6H_4P(O)Ph_2)$. A Schlenk tube was charged with the phosphine oxide alcohol[94] (0.192 g, 0.571 mmol) in 10 mL THF, and 0.0228 g 60% NaH dispersion in mineral oil (0.570 mmol) was added. The mixture was stirred until gas evolution ceased (~20 min). Under an argon flush, 0.200 g $(CpFe(CO)_3)^+PF_6^-$ (0.572 mmol) was added in one portion, giving an orange-red solution. After 4 h of stirring, the mixture was filtered, giving a deep red solution. The infrared spectrum of this solution shows absorptions due to $(CpFe(CO)_2)_2$ impurity, and prominent CO stretches at 2040, 1970, and 1645 cm^{-1} (compare $Cp(CO)_2FeCO_2Me$ reported[100] CO stretches at 2046, 1995, 1665 cm^{-1}).

Preparation of $Cp(CO)_2FeCO_2CH_2P(O)Ph_2$. A Schlenk tube was charged with 0.332 g hydroxymethyldiphenylphosphine oxide[102] (1.43 mmol) and 25 mL dry CH_3CN. Sodium hydride (0.057 g 60% dispersion in mineral oil, 1.42 mmol) was added, and the mixture was stirred for 3 h, when gas evolution ceased, giving a thick white suspension. An additional 10 mL CH_3CN was added to facilitate stirring, then 0.50 g $(CpFe(CO)_3)^+PF_6^-$ (1.43 mmol) in 5 mL CH_3CN as added to the ice-cooled suspension. The mixture was stirred at 0°C for 30 min, then warmed to room temperature and stirred for an additional hour. Filtration afforded a clear red-orange solution.

Solvent was removed in vacuo, then the residue was taken up in 10 mL CH_2Cl_2 and filtered. Solvent removal afforded a red oil which was washed with pentane and thoroughly dried in vacuo, yielding a salmon-colored, hygroscopic, solid foam, 0.580 g: ^{1}H NMR (THF-d_8) δ 4.8 (d, 2H, PC$\underline{H}_2$), 4.92 (s, 5H, Cp), 7.3-7.6 (m, 6H), 7.7-8.0 (m, 4H); ^{31}P NMR (THF-d_8) δ 27.5; IR (THF) ν_{CO} = 2040 (m), 1990 (m), 1950 (s), 1780 (m), 1650 (w) cm^{-1}; IR (KBr) ν_{CO} = 1640 (s, br) cm^{-1}.

Preparation of $[(CO)_4FeCO_2CH_2P(O)Ph_2]^-PPN^+$. Hydroxymethyldiphenylphosphine oxide (0.25 g, 1.08 mmol) was dissolved in 35 mL CH_3CN in a Schlenk tube. Sodium hydride (0.043 g, 60% dispersion in mineral oil, 1.08 mmol) was added, and the mixture was stirred overnight (14 h). The suspension was cooled in an ice bath, and 0.30 mL $Fe(CO)_5$ (d = 1.427, 2.16 mmol) was added via syringe, giving an opalescent yellow solution. After stirring at room temperature for 45 min, the mixture was filtered, and the filtrate was treated with 0.618 g PPN^+Cl^- (1.08 mmol) in 5 mL CH_3CN. Solvent was removed in vacuo; the red residue was taken up in 15 mL CH_2Cl_2 and filtered through Celite. Solvent removal afforded a salmon-colored foam which was washed well with pentane and dried in vacuo, yield 0.732 g. The product is hygroscopic and is insoluble in benzene. ^{1}H NMR (acetone-d_6) δ 4.5 (d, 2H PC$\underline{H}_2$), 7.5-8.2 (m, $\sim$40H, PPN^+ + PPh_2); ^{31}P NMR (THF-d_8) δ 20.7 (PPN^+), 25.2; IR (THF) ν_{CO} = 2000 (w), 1970 (w), 1935 (m), 1910 (s), 1880 (s), 1670 (m) cm^{-1}; IR (KBr) ν_{CO} = 1670 (m) cm^{-1}. Attempted recrystallization from CH_2Cl_2/Et_2O afforded deep red blades; ^{1}H NMR of this product displays no resonances ascribable to the -OC$\underline{H}_2$P(O) unit.

Preparation of $[(CO)_4FeCO_2CH_2CH_2P(O)Ph_2]^-PPN^+$. This complex

was prepared as described above, using the following amounts of materials: hydroxyethyldiphenylphosphine oxide, 0.25 g (1.02 mmol); NaH, 0.0406 g (60% dispersion in mineral oil, 1.02 mmol); $Fe(CO)_5$, 0.280 mL (2.04 mmol); PPN^+Cl^-, 0.583 g (1.02 mmol). Workup as above yielded 0.727 g of a hygroscopic orange-red foam. Spectral data are much as reported above for the hydroxymethyl-derived system: IR (KBr) ν_{CO} = 1670 (m) cm^{-1}.

Preparation of $(CO)_4FeCO_2Me)^-PPN^+$. A solution of 0.15 mL methanol (d = 0.791, 3.7 mmol) in 35 mL CH_3CN was treated with 0.148 g NaH (60% dispersion in mineral oil, 3.7 mmol). After stirring for 3 h, the white suspension was cooled in an ice bath. Iron pentacarbonyl (1.0 mL, 7.3 mmol) was added via syringe in four portions. The orange mixture was warmed to room temperature and stirred for 45 min. A solution of 2.126 g PPN^+Cl^- (3.7 mmol) in 12 mL CH_3CN was added, giving a dense white precipitate; filtration gave an orange solution. Solvent was removed in vacuo, giving an orange microcrystalline solid contaminated with a red oil. The product was washed 2 x 10 mL pentane and 1 x 2 mL CH_3CN and dried in vacuo, yield 0.708 g: ^1H NMR (acetone-d_6) δ 3.4 (s, OCH_3), 7.5-8.1 (m, PPN^+); IR (THF) ν_{CO} = 2020 (w), 1905 (s, br), 1880 (sh), 1620 (m) cm^{-1}; IR (KBr) ν_{CO} = 1610 (m) cm^{-1}.

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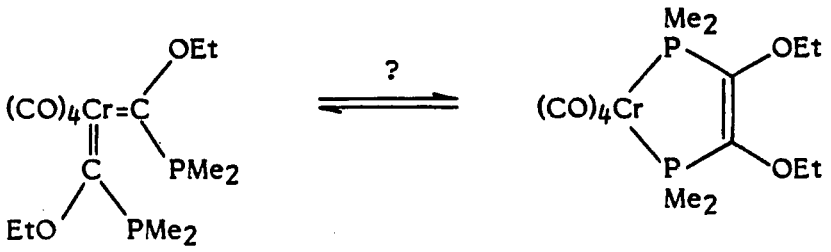

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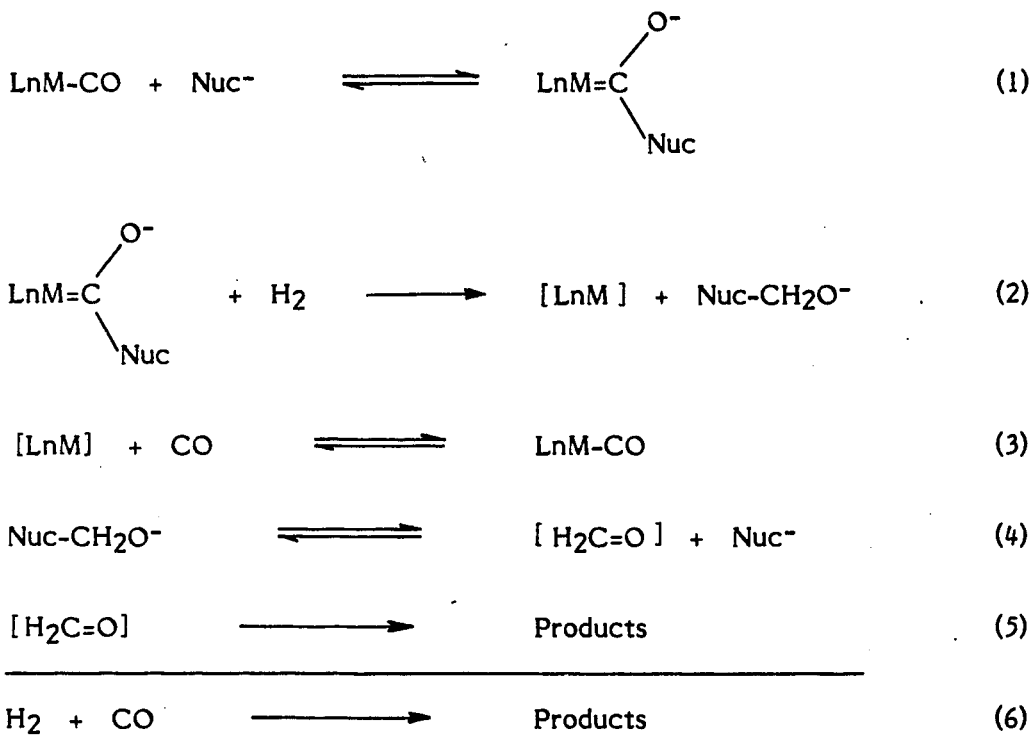
CHAPTER II

Intramolecular Nucleophilic Activation of Carbon Monoxide for Homogeneous Reduction

Introduction

A nucleophile-catalyzed, transition metal mediated homogeneous catalytic reduction of carbon monoxide was discussed in Chapter I. The mechanistic scheme for this proposed catalytic reduction is outlined in equations 1-6.

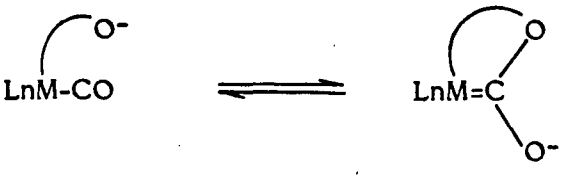


Hydrogenation of mixtures of binary transition metal carbonyl complexes and strong nucleophiles (in particular lithium dimethylamide) generated products derived from the reduction of carbon monoxide to formyl (-CHO) and methyl ($-CH_3$) functionalities.[1] Unfortunately, the activating nucleophile was incorporated in the products of these hydrogenations (N,N-dimethylformamide

and trimethylamine), precluding the recycling of the nucleophile (eq. 4) essential for catalytic operation. Apparently, weaker nucleophiles will be required to permit this regeneration in a catalytic cycle, as they should be more prone to loss from organic intermediates formed in the course of the hydrogenations.

However, weaker nucleophiles show little propensity toward nucleophilic attack at carbon monoxide in neutral transition metal carbonyl complexes. Even alkoxides are incapable of activating carbon monoxide for reduction by hydrogen in binary metal carbonyl systems,[2] apparently due to an unfavorable equilibrium for the required initial nucleophilic attack[2,3] (eq. 1).

The use of functionalized alkoxides, specifically designed to drive this unfavorable equilibrium through follow-up reactions, was discussed in Chapter I. An alternative approach involves the intramolecular delivery of an activating nucleophile, by which the equilibrium for initial nucleophilic attack may be driven entropically in the desired direction.

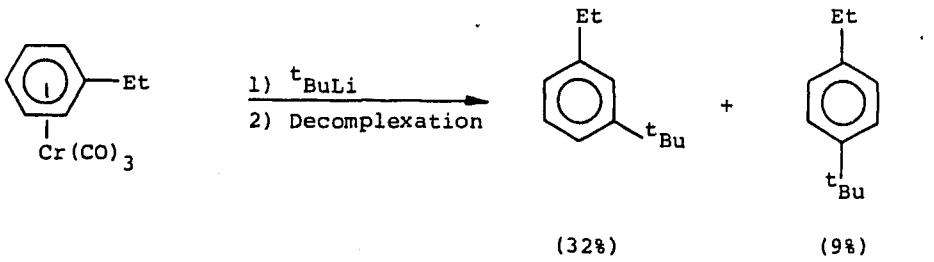


Accordingly, a series of transition metal complexes bearing pendant

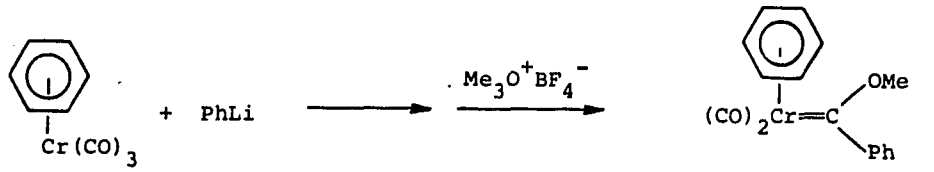
nucleophilic functionalities has been prepared in order to assess the feasibility of this approach.

Results and Discussion

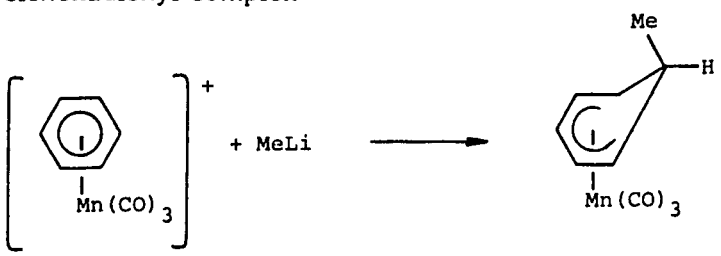
Arene chromium tricarbonyl complexes were chosen for initial investigations, primarily for their ease of synthesis from readily available starting materials and for their high thermal stability.[4,5] Though such complexes often display enhanced reactivity toward nucleophilic substitution at the arene ring[4,6-9]



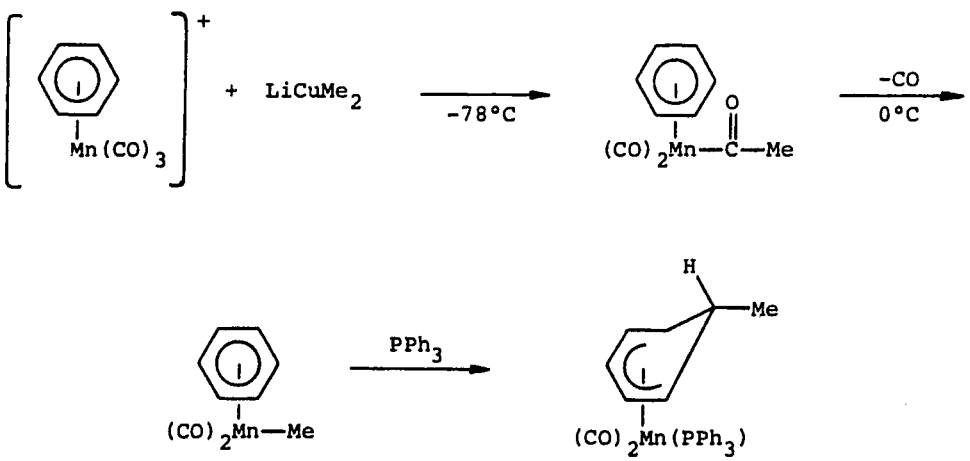
examples of the desired attack by nucleophiles at carbon monoxide are also well-documented.[10-13]



Other potential complications exist in the reactions of arene chromium tricarbonyl complexes with nucleophiles. Thus, under certain conditions, alkyl lithium reagents lithiate the arene ring,[11,13] while frontier molecular orbital calculations[14] suggest the site of initial nucleophilic attack to be the metal atom. In general, the factors governing the experimentally observed sites of nucleophilic attack in such systems are unknown. Similar complications are apparent in the cationic manganese analogs of these complexes; $[(C_6H_6)Mn(CO)_3]^+$ reacts with methyllithium to generate an exo-methylcyclohexadienyl complex[15]

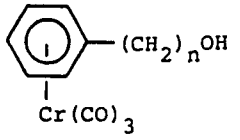


while use of lithium dimethylcuprate as the alkylating agent leads first to a metal acyl complex (via nucleophilic attack at carbon monoxide), then to the endo-methylcyclohexadienyl complex.[16]



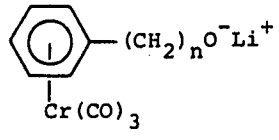
Investigations in this area could thus lead not only to carbon monoxide activating systems, but also to a better understanding of the factors governing nucleophilic attack in arene metal carbonyl complexes.

The functionalized arene chromium tricarbonyl complexes **1-3** were prepared in moderate yield simply by heating equimolar quantities of $Cr(CO)_6$ and the corresponding arene in butyl ether (containing 8% tetrahydrofuran) at reflux (~140°C) for 2-3 days (**2** and **3**) or by heating a solution of $Cr(CO)_6$ in the neat arene for one day (**1**).



	n
1	1
2	2
3	3

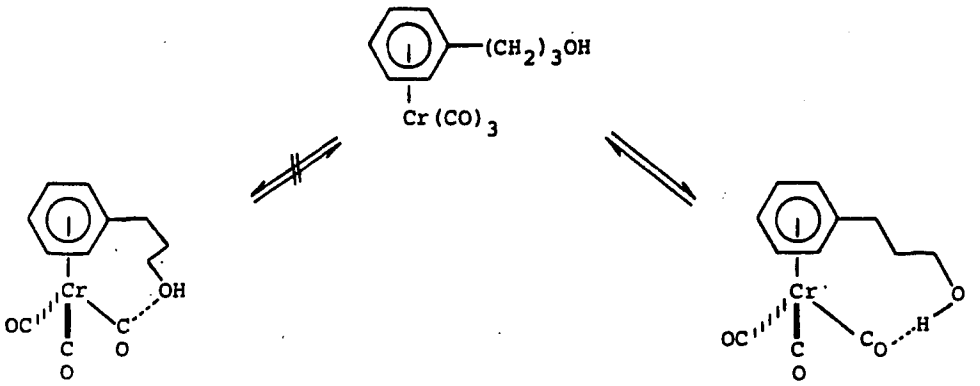
(The hydroxybutylbenzene complex (n = 4) was also prepared; it was obtained as an oil which spontaneously crystallized after ~six months at -20°C, but melted at room temperature. No further studies were performed with this complex.) The lithium salts, **4-6**, were generated by deprotonation of the corresponding alcohols with n-butyllithium.



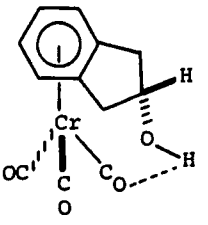
	n
4	1
5	2
6	3

Unfortunately, full physical characterization of complexes **1-6**, through a combination of ^1H NMR, ^{13}C NMR, and infrared spectroscopy, provides no

evidence for any interaction between carbon monoxide and the pendant alcohol or alkoxide, except in complex **3**, which displays an additional carbon monoxide stretching band at lower energy in its infrared spectrum (Figure 1). The disappearance of this band in the deprotonated analog, **6**, however, suggests that it is due to some type of hydrogen bonding to carbonyl oxygen rather than to the desired nucleophilic attack at carbonyl carbon.



Indeed the infrared spectrum of a neat sample of **3** displays no evidence of a free OH stretching mode, while this band is clearly present in the spectrum of complex **2** (Figure 2). Analogous hydrogen bonding has been observed in other arene chromium tricarbonyl complexes,[17] though in these cases, it appeared necessary to force the hydroxyl and $Cr(CO)_3$ groups close together geometrically.



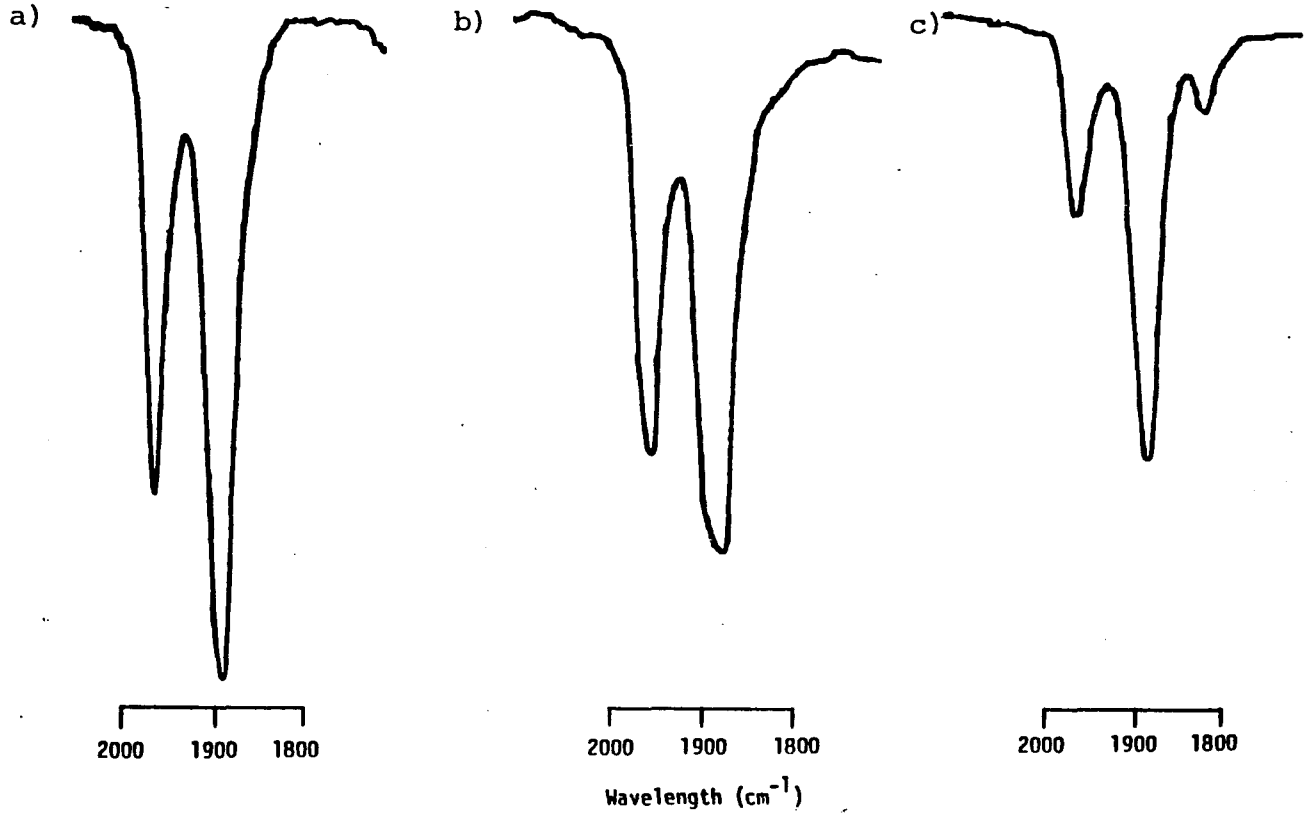


Figure 1. Infrared spectra, dilute THF solution; ν_{CO} region. a) Complex **1**; b) Complex **2**; c) Complex **3**.

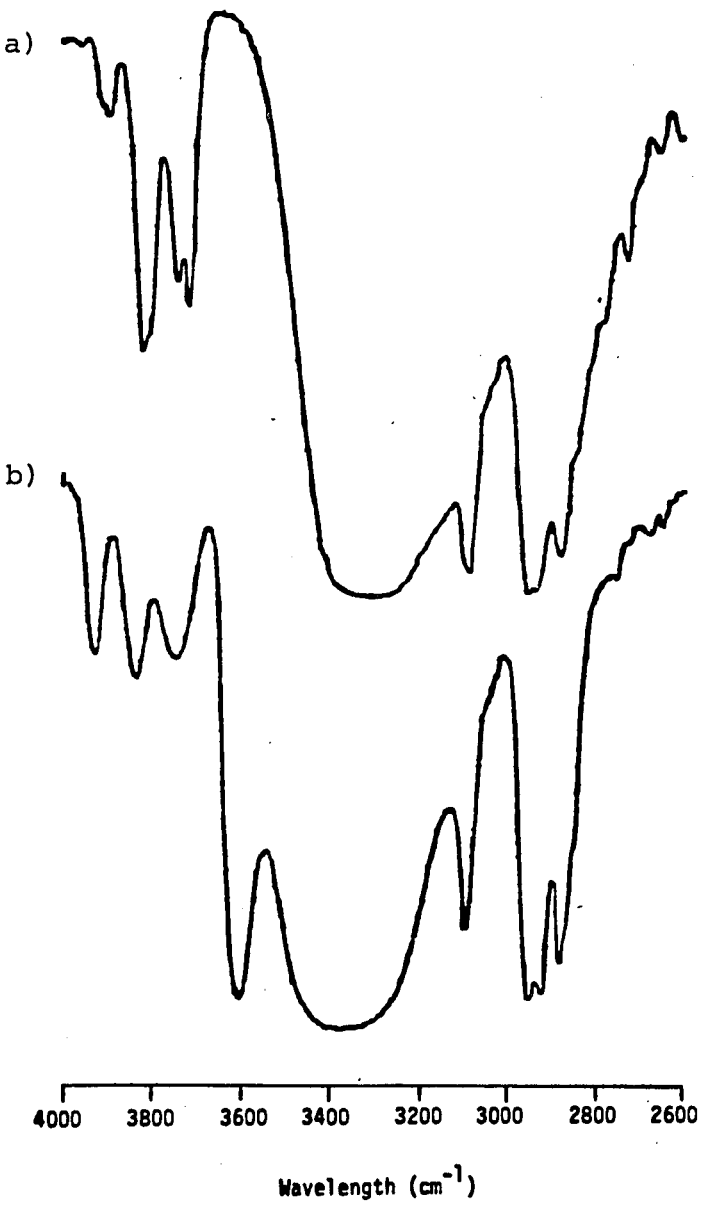
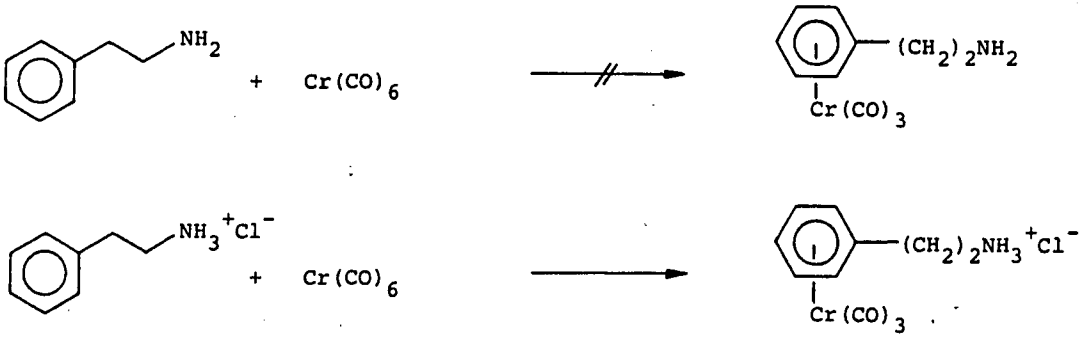


Figure 2. Infrared spectra, neat samples; ν_{OH}, ν_{CH}, and ν_{CO} overtone region. a) Complex **3**; b) Complex **2**.

An amino analog of complex **2**, 2-aminoethylbenzene chromium tricarbonyl, has also been prepared. Attempted synthesis from $Cr(CO)_6$ and β-phenethylamine gave none of the desired complex; however, use of the hydrochloride salt of β-phenethylamine afforded a nearly quantitative yield of the water-soluble hydrochloride salt.

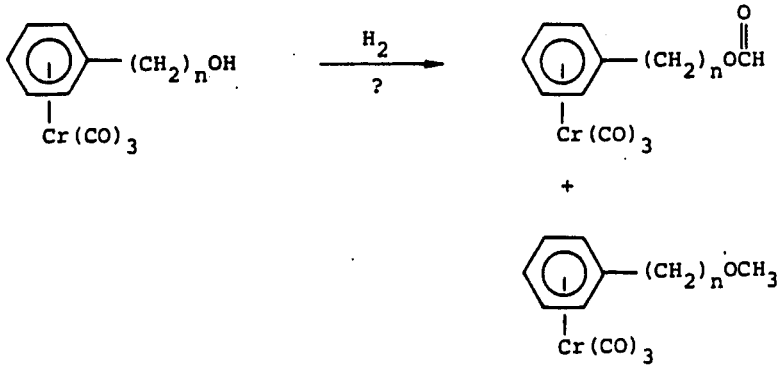


Neutralization with aqueous potassium hydroxide gave the aminoethyl derivative, which displayed an infrared spectrum quite similar to that of complex **3**. The chemistry of this complex was not explored further.

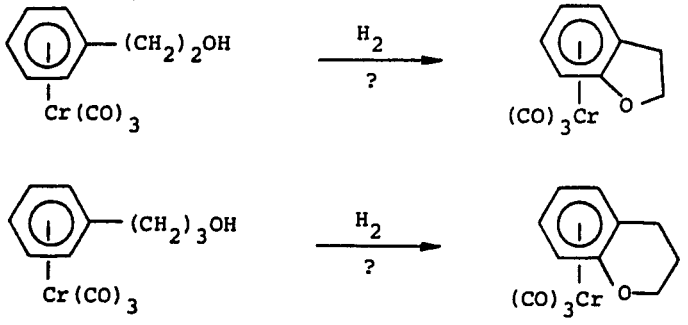
Despite the disheartening spectral observations, the hydrogenations of complexes **1-6** were investigated, under the same mild conditions used in earlier hydrogenations (35 psi H_2, 130°C, hexamethylphosphoric triamide solvent, 24 h). The results of gas chromatographic analyses for carbon monoxide-derived products in these hydrogenations mirrored the apparent lack of activating nucleophilic interactions in the complexes; complexes **1**, **3**, **4**, and **6** gave no volatile products. Though complexes **2** and **5** gave traces of methanol (1% and 2%, respectively, based on starting complex), the amounts obtained were not sufficient to justify the expense of the carbon-13 labeling

experiments necessary to identify carbon monoxide as the source of this methanol.

Given the absence of volatile carbon monoxide-derived products in these hydrogenations, it was necessary to examine the arene fragments of the complexes after hydrogenation, with the expectation of observing products analogous to those derived from the lithium dimethylamide reactions discussed in Chapter I



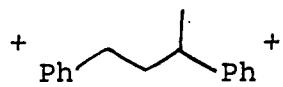
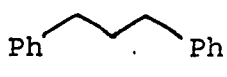
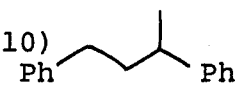
as well as those arising from possible nucleophilic attack at the arene ring.[18]



Analysis for these anticipated products was facilitated by removal of arenes from the chromium tricarbonyl fragment. Oxidative iodination, using the procedure developed by Semmelhack,[20] proved unsatisfactory; test reactions using complex **3** demonstrated the desired release of arene from the complex, but the arene product was not 3-phenyl-1-propanol. (The product has not been identified, but may be the corresponding iodide.) Arene displacement by tributylphosphine in refluxing diglyme[21] appeared to proceed at least semiquantitatively, but the extreme conditions required, together with analytical difficulties posed by the presence of large amounts of high-boiling materials, made this approach undesirable. Fortunately, clean and quantitative arene decomplexation was effected by simply placing a solution of the arene complex hydrogenation mixture (in HMPA), diluted with ether, in air and bright sunlight for one to two hours.[22] Hexamethylphosphoric triamide (HMPA) solvent, which interfered with the gas chromatographic analysis for the anticipated products, was removed by washing a 1,1,1-trichloroethane solution of the products, after arene decomplexation, with several portions of water.

The results of these analyses are presented in Table 1. In the hydrogenation of complexes **1-4** and **6**, unreacted arene was the only organic product detected in significant concentration (Entries 1-4, 6). Complex **5**, in contrast, generated a series of surprising products (Entry 5), identified through a combination of gas chromatography, mass spectrometry, and ^1H NMR analysis of products isolated by preparative scale gas chromatography. These unexpected results were intriguing, and it was felt that a fuller understanding of how these products arose could help define the requirements

Table 1. Hydrogenation Data for Arene Chromium Tricarbonyl Complexes and Control Reactions.[a]

Entry	Complex	Product Yield (%) Recovered $Ph(CH_2)_nOH$	Other
1	$(PhCH_2OH)Cr(CO)_3$ (1)	35	--
2	$[Ph(CH_2)_2OH]Cr(CO)_3$ (2)	26	CH_3OH (1)
3	$[Ph(CH_2)_3OH]Cr(CO)_3$ (3)	38	--
4	$(PhCH_2OLi)Cr(CO)_3$ (4)	26	--
5	$[Ph(CH_2)_2OLi]Cr(CO)_3$ (5)	0	CH_3OH (2) + $PhCH_3$ (25) + $PhCH_2CH_3$ (6) +  (14) +  (12)
6	$[Ph(CH_2)_3OLi]Cr(CO)_3$ (6)	48	--
7	$Ph(CH_2)_2OH$	89	--
8	$Ph(CH_2)_2OLi$	0	$PhCH{=}CH_2$ (45)
9[b]	$Ph(CH_2)_2OLi + Cr(CO)_6$	82	--
10[b]	$(PhCH{=}CH_2)Cr(CO)_3 + LiOH$	0	$PhCH_2CH_3$(85) +  (10)
11[c]	$[Ph(CH_2)_3OH]Cr(CO)_3$ (3)	90	--

[a]All reactions run with 0.5 mmol complex in 3 mL HMPA under 35 psi H_2 at 130°C for 24 h. [b]Run with equimolar quantities of the reactants. [c]No hydrogenation; control to check quantitative reliability of arene decomplexation work-up procedure.

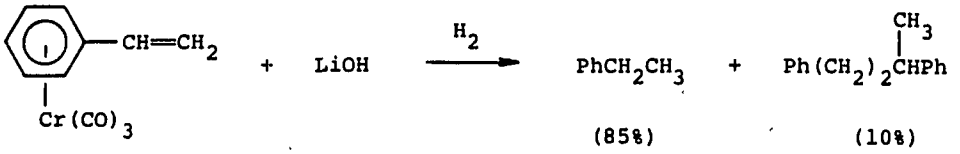
for successful carbon monoxide reduction via intramolecular delivery of an activating nucleophile.

$$5 \xrightarrow{H_2} \underset{(2\%)}{CH_3OH} + \underset{(25\%)}{PhCH_3} + \underset{(6\%)}{PhCH_2CH_3} + \underset{(12\%)}{Ph(CH_2)_3Ph} + \underset{(14\%)}{Ph(CH_2)_2\overset{\overset{CH_3}{|}}{C}HPh}$$

Accordingly, a series of control experiments was run to probe various mechanistic possibilities for the hydrogenation of complex **5**. Uncomplexed phenethyl alcohol is inert to the hydrogenation conditions, being recovered in 89% yield as the only detectable organic product (Entry 7). The lithium salt of phenethyl alcohol, on the other hand, loses the elements of lithium hydroxide and is converted to styrene under the hydrogenation conditions[23] (Entry 8).

$$PhCH_2CH_2O^-Li^+ \xrightarrow[(45\%)]{H_2} PhCH{=}CH_2 \ (+ \ LiOH) \qquad (7)$$

Again, no other organic products are detected, though polystyrene is most likely also present. This suggests the possible intermediacy of styrene chromium tricarbonyl in the formation of the observed products from the hydrogenation of **5**. However, hydrogenation of an equimolar mixture of independently prepared styrene chromium tricarbonyl[25] and lithium hydroxide gives a radically different product distribution (Entry 9)

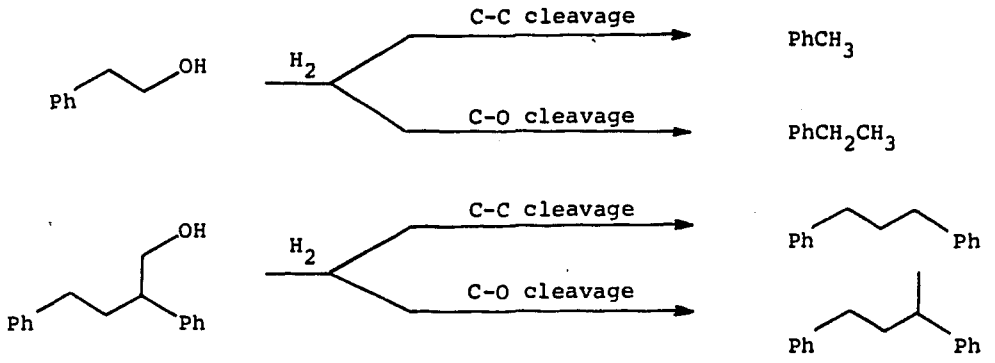


suggesting the unlikelihood of this mechanistic possibility. Finally, hydrogenation of an equimolar mixture of $Cr(CO)_6$ and the lithium salt of phenethyl alcohol gives neither styrene nor any of the other anticipated products, but only the protonated alcohol (Entry 10; vide infra).

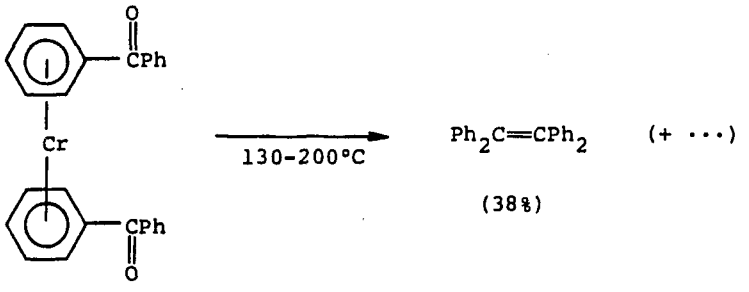
$$PhCH_2CH_2O^- + Cr(CO)_6 \xrightarrow{H_2} PhCH_2CH_2OH \qquad (8)$$

Though key mechanistic details are lacking, the observations on the hydrogenation of **5** presented above are perhaps best summarized by invoking an initial Guerbet-type condensation[26]

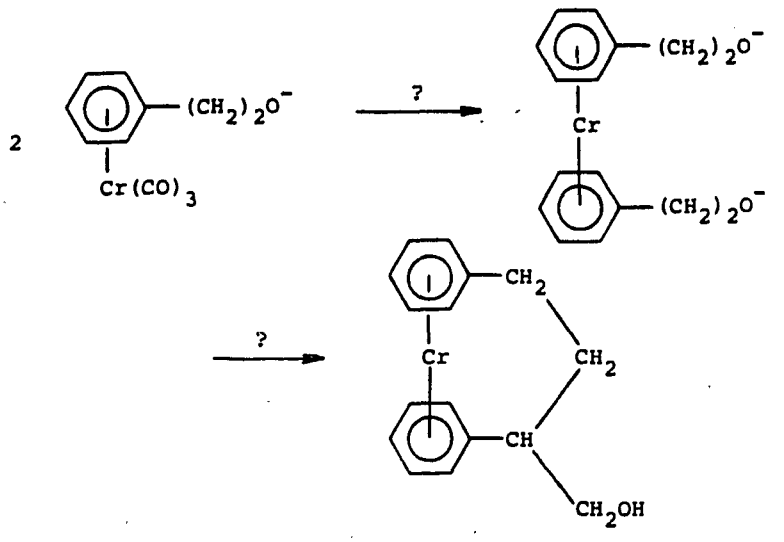
coupled with chromium-mediated hydrogenolyses of carbon-carbon and carbon-oxygen bonds in the starting and product alcohols (chemistry well-precedented in β-phenylethanol systems[27]).



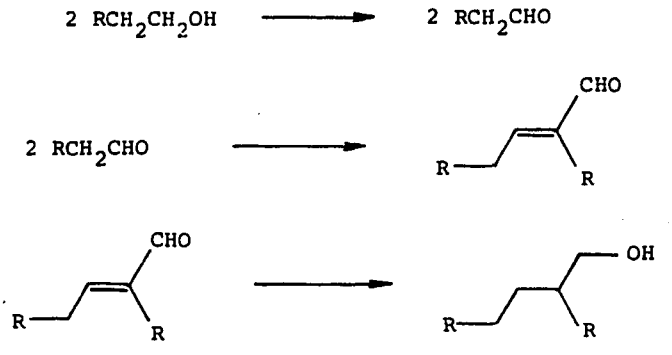
A recently reported reductive ligand coupling in a bis(π-arene)chromium complex[28] may possibly be mechanistically related to this system.



This coupling is strictly an intramolecular reaction; no intermolecular cross-over is observed even though the reaction is carried out in neat complex (no solvent). Perhaps ligand coupling in complex **5** occurs via intermediate formation of a bis(arene) complex, which could set up the proper geometry to allow Guerbet-type condensation under uncharacteristically mild conditions.

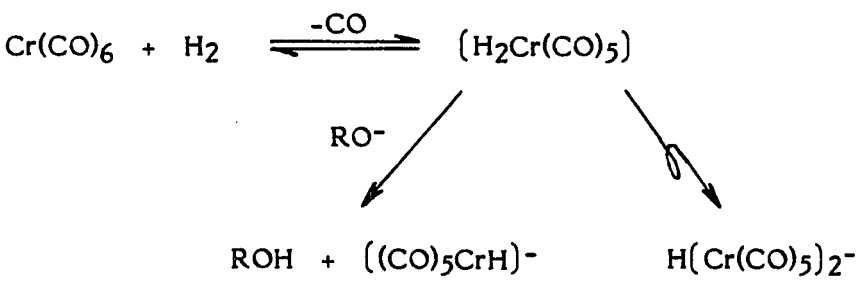


Alternately, the condensation may be facilitated by the presence of chromium "redox reservoirs", which could allow the proposed intermediate redox chemistry in the Guerbet reaction[26] to occur under mild conditions.[29]



The simple protonation of the lithium salt of phenethyl alcohol upon hydrogenation in the presence of $Cr(CO)_6$ (eq. 8), in contrast to the formation of styrene observed in the absence of $Cr(CO)_6$ (eq. 7), was quite surprising, and this reaction was examined in greater detail. The infrared spectrum of an aliquot of the reaction mixture displayed prominent absorptions at 1890 and

1860 cm^{-1}; the shapes and intensities of these bands match those reported by Darensbourg for the $[(CO)_5CrH]^-$ anion[30] (Figure 3). In addition, a hydride resonance at approximately -7 ppm (vs TMS) was observed in the ^1H NMR spectrum of the neat reaction mixture, again matching that reported by Darensbourg for the $[(CO)_5CrH^-]$ anion.[30] Hydrogenation of $Cr(CO)_6$ in the absence of added alkoxide yielded an orange solution; the infrared spectrum of this solution (Fig. 3) suggests the presence of $H[Cr(CO)_5]_2^-$.[30] A hydride resonance at approximately -20 ppm, as expected for this bridging hydride anion,[30] was observed in the ^1H NMR spectrum of the neat reaction mixture. These observations are wholly consistent with intermediate formation of an acidic chromium dihydride[31,32] which may either be deprotonated to the mononuclear hydride anion or, in the absence of a suitable base, collapse to the bridging hydride anion (the "thermodynamic sink" in chromium carbonyl hydride chemistry[30]).



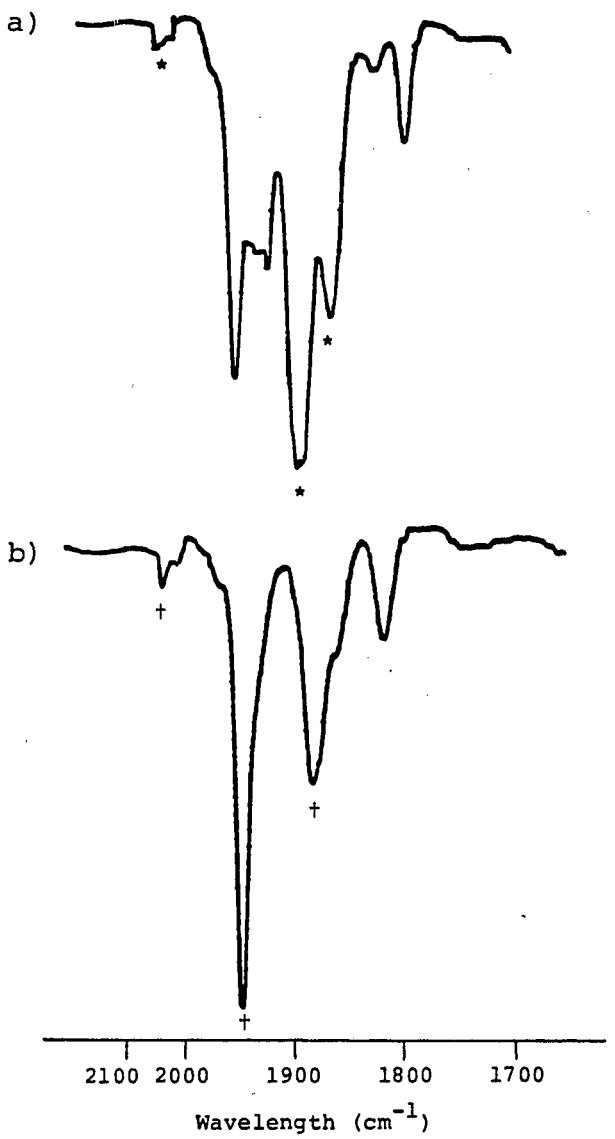


Figure 3. Infrared spectra, HMPA solution, νCO region. a) $Cr(CO)_6 + H_2 + PhCH_2CH_2O^-Li^+$; b) $Cr(CO)_6 + H_2$.

*Bands due to $[(CO)_5CrH]^-$
†Bands due to $[(CO)_5Cr]_2H^-$

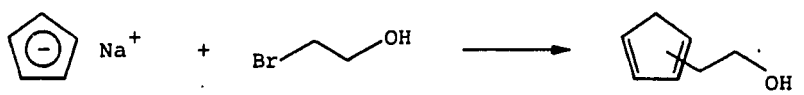
Summary and Conclusions

The hydrogenation of a series of arene chromium tricarbonyl complexes bearing pendant alcohol or alkoxide functionality under mild conditions (35 psi H_2, 130°C, HMPA solvent, 24 h) has been examined in detail. The results of these hydrogenations and the physical characterizations of these complexes provide no evidence for intramolecular nucleophilic attack by alcohol or alkoxide at carbon monoxide. A range of interesting products is obtained from the hydrogenation of (lithium 2-phenylethoxide) chromium tricarbonyl, complex **5**; these products most likely arise from reductive couplings and fragmentations of the arene ligand rather than from nucleophilic attack at carbon monoxide. These results taken together suggest that successful design of bifunctional catalysts for the homogeneous reduction of carbon monoxide will require the combination of carbonyl complexes highly activated toward nucleophilic attack (most likely cationic carbonyl complexes) with relatively weak nucleophiles (perhaps alcohols or tertiary amines) delivered via chemical links resistant to hydrogenolysis.

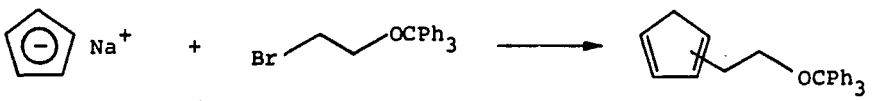
Finally, the direct reaction between $Cr(CO)_6$ and molecular hydrogen under mild conditions has been observed. The intermediate dihydride produced, $H_2Cr(CO)_5$, may be deprotonated by added alkoxides to give the mononuclear hydride anion, $[(CO)_5CrH]^-$, or it may be allowed to collapse to the more stable bridging hydride, $H[Cr(CO)_5]_2^-$. These results not only bear on Fischer-Tropsch related reaction chemistry,[32] but also suggest a possible entry into organic homogeneous catalytic reduction chemistry. Thus, if the $[(CO)_5CrH]^-$ anion proves to be capable of catalytic reductions of organic functionalities (c.f. Chapter I), these reductions may possibly be run

using $Cr(CO)_6$ and a catalytic amount of base rather than with the more difficult to prepare $(HCr(CO)_5)^-$.

Some consideration was given to the use of functionalized cyclopentadienyl metal carbonyl complexes to investigate the intramolecular delivery of nucleophiles to transition metal bound carbon monoxide. These investigations led to an improved synthesis[33] of hydroxyethylcyclopentadiene, wherein excess cyclopentadienyl sodium is quenched as rapidly as possible with 2-bromoethanol, affording the desired alcohol in ∿30% yield after vacuum distillation.

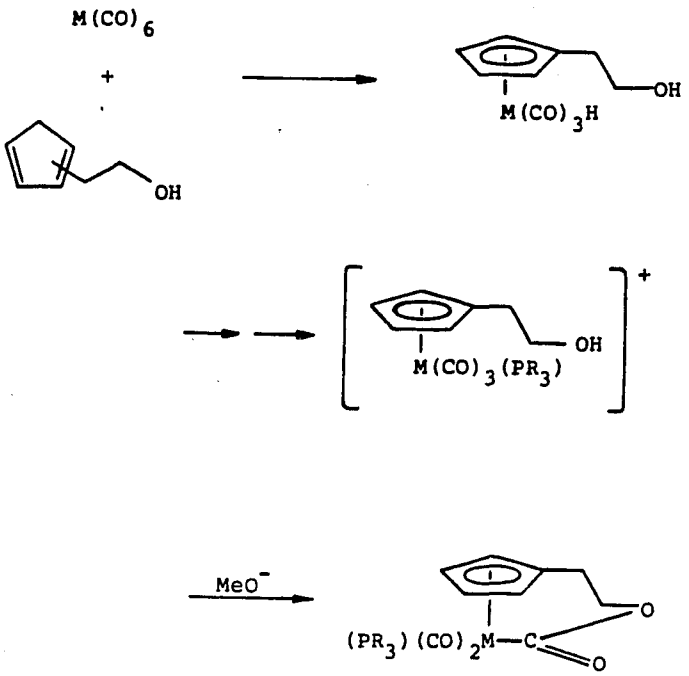


Substitution of the triphenylmethyl (trityl) ether of bromoethanol was found to increase the yield to ∿50% (after preparative thin layer chromatography).



The details of these preparations are presented in the Experimental Section. Though attempts to prepare the manganese tricarbonyl complexes of these cyclopentadienes failed, giving either paramagnetic oils or insoluble powders, the compounds are presently being elaborated into molybdenum and tungsten

carbonyl systems which incorporate at least some of the features deemed necessary for successful carbon monoxide activation and reduction.[34]



Experimental Section

Materials. Arene chromium tricarbonyl complexes were prepared by the general method of Mahaffy and Pauson[5] and were treated as air sensitive, using standard techniques, until isolated as crystalline solids. Tetrahydrofuran (THF), toluene, and hexane were dried over sodium/benzophenone ketyl and vacuum transferred before use. Dichloromethane was dried over CaH_2 and vacuum transferred. Butyl ether was refluxed over $LiAlH_4$ and distilled, under argon, onto Linde 4A molecular sieves. Hexamethylphosphoric triamide (HMPA) was pre-dried over CaH_2, vacuum distilled onto sodium metal, and finally vacuum distilled onto activated Linde 4A molecular sieves and stored in an inert atmosphere box. $Cr(CO)_6$ was obtained from Pressure Chemical Co. (Pittsburgh, PA). Benzyl alcohol, phenethyl alcohol, 3-phenyl-1-propanol, 4-phenyl-1-butanol, and phenethylamine were obtained from Aldrich Chemical Co. E. Merck 70-230 mesh silica gel was used for chromatographic purifications. Styrene chromium tricarbonyl was prepared as described.[25] The lithium salt of phenethyl alcohol was precipitated from a hexane solution of the alcohol (under argon) upon addition of n-butyllithium and was stored in the drybox. Phenethylamine hydrochloride was precipitated from an ether solution of the amine upon bubbling with dry HCl gas and was recrystallized from absolute ethanol. Standards for gas chromatography were prepared as follows and purified by preparative scale gas chromatography on an 8-ft 5% SE-30 column: 2,3-dihydrobenzofuran, atmospheric hydrogenation of 2,3-dihydrobenzofuran-3-one[35]; 2,3-dihydrobenzopyran, $AlCl_3$ cyclization of 1,3-diphenoxypropane[36]; 1,3-diphenylpropane, Wurtz coupling of bromobenzene

and 1,3-dibromopropane[37]; 1,3-diphenylbutane, atmospheric hydrogenation of 1,3-diphenyl-3-butanol[38]; formates: reflux of corresponding alcohol 18 h in 98% HCO_2H; methyl ethers: alkylation of sodium salts of corresponding alcohols with CH_3I.

Hydroxymethylbenzene Chromium Tricarbonyl, 1.[39] A 100 mL three-neck round-bottom flask, equipped with a magnetic stir bar, argon inlet, straight-bore condenser, and oil bubbler, was charged with 40 mL benzyl alcohol. The alcohol was degassed in vacuo, then, under an argon flush, 4.0 g $Cr(CO)_6$ (18.2 mmol) and 10 mL THF were added. The solution was brought to reflux; a yellow color gradually developed. Sublimed $Cr(CO)_6$ was periodically washed back into the solution by turning off the cooling water for a few minutes. Reflux was continued for 22 h. The solution was cooled under argon, diluted with 50 mL ether, and filtered through a 1" x 2" pad of degassed silica, washing with 3 x 5 mL ether. A trace of green material was left on the silica. The yellow filtrate was brought to dryness in vacuo, with gentle heating, leaving a yellow crystalline mass. Recrystallization from 80 mL toluene afforded 2.93 g (66%) bright yellow, fibrous crystals, mp 90.7-91.8°C (lit[39] 95.5-96.5°C): ^1H NMR (acetone-d_6) δ 4.3-4.7 (m, 3H, $-C\underline{H}_2O\underline{H}$), 5.4-5.8 (m, 5H, Ph); IR (THF): νCO = 1890, 1965 cm^{-1}.

Hydroxyethylbenzene Chromium Tricarbonyl, 2.[17] An argon-flushed 250 mL three-neck round-bottom flask, equipped with an argon inlet, reflux condenser, and oil bubbler, was charged with 4.0 g $Cr(CO)_6$ (18.2 mmol), 2.17 mL phenethyl alcohol (d = 1.023, 18.2 mmol), 120 mL butyl ether, and 10 mL THF. The colorless suspension was heated to reflux. Reflux was maintained for 72 h, giving a bright yellow solution containing traces of a green solid.

The solution was cooled under argon and filtered through a 1" x 2" pad of silica; adhering material was washed through with a few small portions of THF, leaving a green band on the silica. Removal of solvents in vacuo, with gentle heating, gave an orange oil which solidified to a crystalline mass. Recrystallization from toluene/hexane at 0°C gave long yellow needles, yield 3.1 g (66%), mp 49.7-51.3°C (lit[17] 51-52°C): ^{1}H NMR (acetone-d_6) δ 2.55 (t, 2H, PhC$\underline{H}_2$-), 3.78 (t, 2H, -C$\underline{H}_2$OH), 3.98 (s, 1H, -O$\underline{H}$), 5.3-5.7 (m, 5H, Ph); ^{13}C NMR (acetone-d_6) δ 38.9, 62.8 (-CH_2CH_2), 92.6, 95.4, 95.8, 113.0 (Ph), 234.7 (CO); IR (THF): ν_{CO} = 1880, 1956 cm^{-1}; IR (neat): ν_{OH} = 3300-3420 (s, br, H-bonded), 3600 (s, free OH) cm^{-1}.

Hydroxypropylbenzene Chromium Tricarbonyl, 3. This complex was prepared as described above for **2**, substituting 2.46 mL 3-phenyl-1-propanol (d = 1.008, 18.2 mmol) for phenethyl alcohol. Reflux was continued for 39 h. Crystallization from 35 mL toluene at -50°C afforded 2.95 g (60%) of yellow needles, mp 74.9-76.1°C: ^{1}H NMR (acetone-d_6) δ 1.8 (m, 2H, -CH_2C$\underline{H}_2$$CH_2$-), 2.5 (m, 2H, PhC$\underline{H}_2$-), 3.6 (broad t, 3H, -C$\underline{H}_2O\underline{H}$), 5.6 (m, 5H, Ph); ^{13}C NMR (acetone-d_6) δ 32.1, 34.9, 61.2 (-$CH_2CH_2CH_2$-), 92.4, 94.7, 95.8, 115.7 (Ph), 234.6 (CO); IR (THF): ν_{CO} = 1810, 1880, 1956 cm^{-1}; IR (neat): ν_{OH} = 3260-3360 (s, br) cm^{-1}.

Anal. calcd. for $C_{12}H_{12}CrO_4$: C, 52.95; H, 4.44; Cr, 19.10. Found: C, 53.23; H, 4.43; Cr, 18.77.

(Lithium Phenylmethoxide) Chromium Tricarbonyl, 4. Complex **1** (1.0 g, 4.1 mmol) was dissolved in 25 mL THF under argon. n-Butyllithium (in hexane, 1.6 M, 2.56 mL, 4.1 mmol) was added slowly via syringe. The resulting solution was stirred 15 min at room temperature, then filtered

under argon. Solvent was removed in vacuo, giving an orange-yellow foam. The solid was scraped out and bottled in the inert atmosphere box, yield 0.74 g (72%). Spectral properties are identical to those of complex **1**, with the exception of the loss of features due to the O-H unit.

(Lithium 2-Phenylethoxide) Chromium Tricarbonyl, 5. Complex **2** (1.0 g, 3.87 mmol) was dissolved in 30 mL THF under argon. n-Butyllithium (in hexane, 1.6 M, 2.42 mL, 3.87 mmol) was added slowly via syringe. The solution was stirred 20 min at room temperature, then solvent was removed in vacuo, giving an orange-yellow gum. This was taken up in 10 mL THF, 15 mL toluene was added, and the volume was reduced to approximately 3 mL. Additional toluene (5 mL) was added, and the volume was again reduced to 3 mL. Solvent was decanted from the precipitated solid; the solid was washed with 5 mL toluene, then dried in vacuo. The yellow powder was scraped out and bottled in the inert atmosphere box, yield 0.975 g (95%). Spectral properties are identical to those of complex **2**, with the exception of the loss of features due to the O-H unit.

(Lithium 3-Phenylpropoxide) Chromium Tricarbonyl, 6. This complex was prepared as described above for complex **5**, on a 1.0 g (3.7 mmol) scale. The product precipitated as an oil which, when dried in vacuo, solidified to a bright yellow foam, yield 0.86 g (84%). IR (THF): νCO = 1890, 1965 cm^{-1}. Other spectral properties are identical to those of complex **3**, with the exception of the loss of features due to the O-H unit.

General Hydrogenation Procedure. In the inert atmosphere drybox, a glass pressure bottle with a magnetic stir bar was charged with 0.5 mmol of the arene chromium tricarbonyl complex and 3 mL HMPA. The bottle was

sealed to a pressure head, using a Neoprene O-ring, bearing a pressure gauge, an inlet needle valve, and a ball valve capped with a rubber septum (for gas sampling). The assembly was removed from the drybox and connected to a hydrogen source. After repeatedly filling the bottle to 35 psi H_2 and venting through the ball valve, the bottle was pressured to 35 psi H_2, sealed, and placed in a 130°C oil bath (bottom few inches of the bottle). Reactions were run for 24 h; solutions appeared to remain homogeneous.

Gas Chromatographic Analysis. Analyses were carried out on a Varian model 1440 instrument (injector temperature 210°C, detector temperature 240°C, N_2 carrier, 50 psi inlet pressure, 40 mL/min flow rate) linked to a Hewlett Packard model 3390A reporting integrator. Vapors and solutions were analyzed for volatile products on a 9-ft Porapak Q column at 110°C and on an 8-ft 3% SE-52/Chrom G AWDMCS column temperature programmed from 60-200°C at 15°C/min. After initial analyses, the solution was transferred to a beaker (in air), diluted with 200 mL ether, and placed in direct sunlight until completely decolorized (1-2 h). Ether was removed on a rotary evaporator; the residue was taken up in 50 mL H_2O and extracted 3 x 20 mL CH_3CCl_3. The combined organics were washed 3 x 25 mL H_2O and filtered through $MgSO_4$. Solvent was removed on a rotary evaporator, and the residue was taken up in 5 mL ether and transferred to a stoppered vial. This solution was then analyzed on the SE-52 column. Appropriate blanks were run to identify peaks due to the rather involved workup procedure. Yields were determined by internal standard addition, using either 1,3-diphenylpropane, 1,3-diphenylbutane, or phenethyl formate, as appropriate.

Preparative Scale Hydrogenation of Complex 5. Complex 5 (0.685 g,

2.6 mmol) was dissolved in 16 mL HMPA and stirred at 130°C under 35 psi H_2 for 24 h. The red solution was transferred to a beaker, diluted with 300 mL ether, and placed in direct sunlight for 2 h, then worked up as described above, giving a fragrant oil. Two major peaks at long retention time on the SE-52 column were observed. These peaks were separated by preparative gas chromatography (¼" x 8' 5% SE-30, 150°C, injector temperature 210°C, detector temperature 250°C, He carrier, 26 psi inlet pressure, 50 mL/min flow rate), collecting in dry ice/acetone cooled traps. Mass spectral analysis yielded molecular weights of 196 and 210 for the two products. 90 MHz FT NMR spectra were recorded on a JEOL FX-90Q instrument on CCl_4 solutions of the products in 1.7 mm microtubes. All spectral details were identical to those for independently prepared authentic samples of 1,3-diphenylpropane and 1,3-diphenylbutane.

Hydroxybutylbenzene Chromium Tricarbonyl. This complex was prepared as described above for complex **2**, substituting 2.73 g 4-phenyl-1-butanol (18.2 mmol) for phenethyl alcohol. Reflux was continued for 42 h. Precipitation from toluene/hexane gave a bright yellow oil which was washed 3 x 5 mL hexane, dried in vacuo, and stored at -20°C. After ~6 months, the oil spontaneously crystallized, giving a solid yellow mass. The solid melts at room temperature.

2-Aminoethylbenzene Chromium Tricarbonyl Hydrochloride. This complex was prepared as described above for complex **2**, on half the scale, substituting 1.433 g β-phenethylamine hydrochloride (9.1 mmol) for phenethyl alcohol. Reflux was continued for 16 h, giving a yellow suspension. The mixture was filtered under argon, and the solid was washed 2 x 10 mL butyl

ether and thoroughly dried in vacuo, yield 2.46 g (92%) yellow powder: ^{1}H NMR (D_2O) δ 2.5 (m, 2H, PhC$\underline{H_2}$-), 3.0 (m, 2H, -C$\underline{H_2}NH_3^+$), 5.3 (m, 5H, Ph).

2-Hydroxyethylcyclopentadiene. A 100 mL three-neck round-bottom flask was charged with 7.68 g NaH (50% dispersion in mineral oil, 0.16 mol) and a stir bar. The flask was connected to an argon manifold and a bubbler, and 50 mL THF was added. With ice water cooling, 13.2 mL freshly distilled cyclopentadiene (d = 0.802, 10.6 g, 0.16 mol) was slowly syringed in. The mixture was allowed to warm to room temperature and stirred for 1 h. With cooling in an ice bath and good stirring, bromoethanol (10.0 g, 0.08 mol) was added as quickly as possible (exothermic!), giving a dense white precipitate and a violet solution. After stirring under argon for 12 h, the flask was opened to air. Petroleum ether (50 mL) was added, and the resulting suspension was washed 2 x 75 mL H_2O, giving a yellow organic phase and a red-brown aqueous phase. The aqueous phase was extracted 4 x 30 mL petroleum ether, and the combined organics were dried over Na_2SO_4. TLC on silica gel, eluting with 2:1 petroleum ether/ethyl acetate (UV visualization) showed only one major spot (R_f ~0.35). Solvent was removed on a rotary evaporator, and the resulting brown oil was vacuum distilled, yielding approximately 3 g (30%) of a colorless oil, bp 50-55°C/1.5-2 mm, stored at -50°C to prevent dimerization: ^{1}H NMR ($CDCl_3$) δ 2.65 (m, 3H), 2.9 (m, 2H), 3.7 (broad m, 2H), 6.25 (m, 3H). This reaction has been repeated on a 0.5 mol scale, giving a comparable yield of product.

Attempted Preparation of Hydroxyethylcyclopentadienylmanganese Tricarbonyl. A 100 mL three-neck round-bottom flask was charged with 0.065 g NaH (50% dispersion in mineral oil, 1.36 mmol) and 25 mL THF.

Hydroxyethylcyclopentadiene (0.15 g, 1.36 mmol) was added in one portion; gas evolution was immediate, and the solution gradually became yellow. Stirring for 2 h at room temperature gave a pale yellow suspension. Addition of $ClMn(CO)_5$[40] (1.36 mmol) resulted in immediate gas evolution and a color change from yellow to orange. On stirring, a white solid precipitated. After 1 h, filtration under argon, followed by removal of solvent in vacuo, gave a yellow solid and an orange oil. The ^1H NMR spectra of both products were broad and uninterpretable.

2-Triphenylmethoxyethylcyclopentadiene. The trityl ether of bromoethanol was prepared from equimolar amounts of the alcohol and triphenylmethyl chloride in pyridine, stirring ~16 h and recrystallizing the product (after aqueous extraction to remove pyridine and pyridinium chloride) from absolute methanol. NaH (1.225 g 50% dispersion in mineral oil, 0.026 mol) was suspended in 500 mL THF in a 1 ℓ side-arm round-bottom flask under argon. The mixture was cooled to 0°C, and freshly cracked cyclopentadiene (2.10 mL, d = 0.802, 1.69 g, 0.026 mol) was added via syringe. Two hours of stirring at room temperature gave a very pale yellow solution. The solution was cooled to -78°C, and the trityl ether of bromoethanol (7.5 g, 0.020 mol) was added in one portion. The mixture was warmed to room temperature over the course of ~20 min; the pale orange solution gradually darkened and deposited a white solid. The reaction was monitored by TLC -- an aliquot of the solution was removed, quenched with H_2O, mixed with petroleum ether, and spotted on a silica TLC plate. Three elutions with petroleum ether were used to develop the plate; visualization was effected with a UV lamp. Under these conditions, the product moves slightly behind

the starting trityl ether (R_f ~0.3). Stirring was continued for ~5 days, after which time only a trace of starting material was left. The volume was reduced to 100 mL in vacuo, then 100 mL petroleum ether and 60 mL H_2O were added. The yellow organic layer was separated, and the aqueous phase was extracted 3 x 60 mL petroleum ether. The combined organics were dried over Na_2SO_4, then solvent was removed in vacuo, giving ~8 g of a brown oil. Preparative TLC on 2 mm silica plates, eluting three times with petroleum ether, collecting the leading major band and extracting the product with ether, afforded 3.3 g white crystalline product (46%): ^1H NMR ($CDCl_3$) δ 2.5-3.6 (m, 6H), 6.0-6.5 (m, 3H), 7.0-7.5 (m, 15H).

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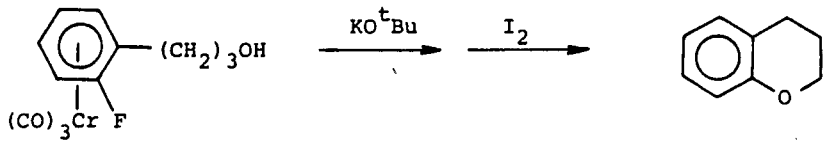

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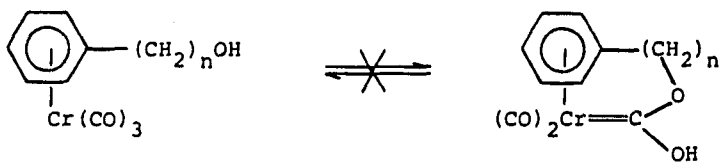
CHAPTER III

Electrochemical Oxidation of Arene Chromium Tricarbonyl and Arene Tungsten Tricarbonyl Complexes

Introduction

The intramolecular delivery of activating nucleophiles to transition metal bound carbon monoxide was discussed in Chapter II. In the series of hydroxyalkylbenzene chromium tricarbonyl complexes examined, no physical or chemical evidence for the desired nucleophilic attack by alcohol or alkoxide was obtained.

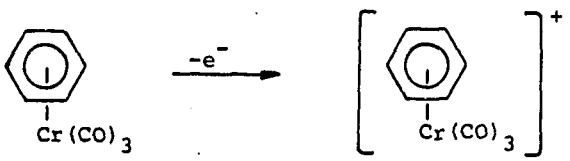


Cationic metal carbonyl complexes are, in general, much more susceptible to nucleophilic attack at carbon monoxide than are neutral complexes,[1-6] and it was felt the cations derived from the hydroxyalkylbenzene chromium tricarbonyl complexes might display the desired behavior.

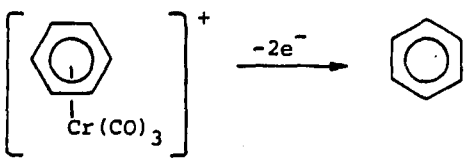
Unfortunately, chemical oxidation of arene chromium tricarbonyl complexes is well-known to result in multi-electron processes,[7,8] leading to irreversible loss of the arene from the complex. The electrochemical oxidation of these complexes appeared to offer promise of selective one-electron oxidation,[9-12]

potentially affording the desired functionalized cationic complexes. Accordingly, the cyclic voltammetric oxidation of the arene chromium tricarbonyl complexes was investigated.

Though the oxidation chemistry of such chromium complexes has attracted considerable interest,[9-11,13,14] mechanistic details of the complex chemistry observed are lacking. At the current level of understanding,[13] initial one-electron oxidation of the chromium complex (eq. 1) is followed by rapid loss of ligands and further oxidation (eq. 2), the latter presumably a multistep process of unknown mechanism.



(1)



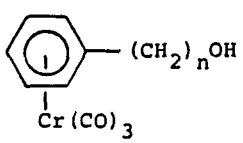
(2)

The results of the one-electron electrochemical oxidations of a series of functionalized and unfunctionalized arene chromium tricarbonyl complexes, discussed in detail below, have not led to the desired new insights into carbon monoxide reduction chemistry, but have significantly contributed to a fuller understanding of the mechanistic complexities of these systems.

Extension of these investigations to the corresponding tungsten complexes has led not only to a better understanding of the behavior of the chromium systems, but also to a finding of fundamental significance in the general area of odd-electron organometallic reaction chemistry. Thus, expanded coordination sphere complexes analogous to those currently proposed as intermediates in associative mechanisms[15-17] for electrocatalytic ligand substitution have been electrochemically generated and observed, thereby vividly demonstrating the feasibility of such intermediates. The results of these studies are detailed below.

Results and Discussion

Hydroxyethylbenzene chromium tricarbonyl (1) and hydroxypropylbenzene chromium tricarbonyl (2)



1 n = 2
2 n = 3

each display electrochemical oxidations at approximately +0.7 V (vs Ag/AgCl, Pt disc electrode, 1 mM solutions in acetonitrile, 0.1 M tetraethylammonium perchlorate (TEAP) supporting electrolyte, 25°C) that are completely irreversible on the cyclic voltammetric time scale, even at scan rates as high as 50 V/sec. Bulk electrolysis of complex **2** at +0.8 V demonstrates that the

oxidation is an overall one electron process, and also provides a possible explanation for the observed irreversibility -- the initially yellow solution of **2** turns green (indicative of Cr(III)), and gas chromatographic analysis of the resulting solution confirms the presence of free 3-phenyl-1-propanol. Oxidation of complexes **1** and **2**, therefore, appears to result simply in rapid decomposition; no products derived from nucleophilic attack by the pendant alcohol functionality at either carbon monoxide or the arene ring are formed.

As the source of the observed instability of the cations generated from the functionalized chromium complexes was not obvious, the oxidation of unfunctionalized analogs was investigated; an understanding of the stability and reaction chemistry of these complexes would then permit conclusions about the effects of pendant functionality to be drawn. The parent complex, benzene chromium tricarbonyl, displays electrochemical behavior quite similar to that of complexes **1** and **2** (Fig. 1). This electrochemical irreversibility of the oxidation of simple arene chromium tricarbonyl derivatives due to rapid irreversible follow-up chemical reactions has been previously noted;[9-11,13] until recently,[9,13] however, conclusive evidence that decomposition of the oxidation product involves decomplexation of the arene was not presented.[18]

The few reports available on the chemical[19-21] and electrochemical[9-12] generation of relatively stable cations from arene metal tricarbonyl complexes suggest that polyalkylation of the arene ring results in increased stability; thus, chemical oxidation of hexamethylbenzene tungsten tricarbonyl yielded a crystalline product[19] whereas the analogous product from benzene tungsten tricarbonyl proved too unstable to isolate. It has been

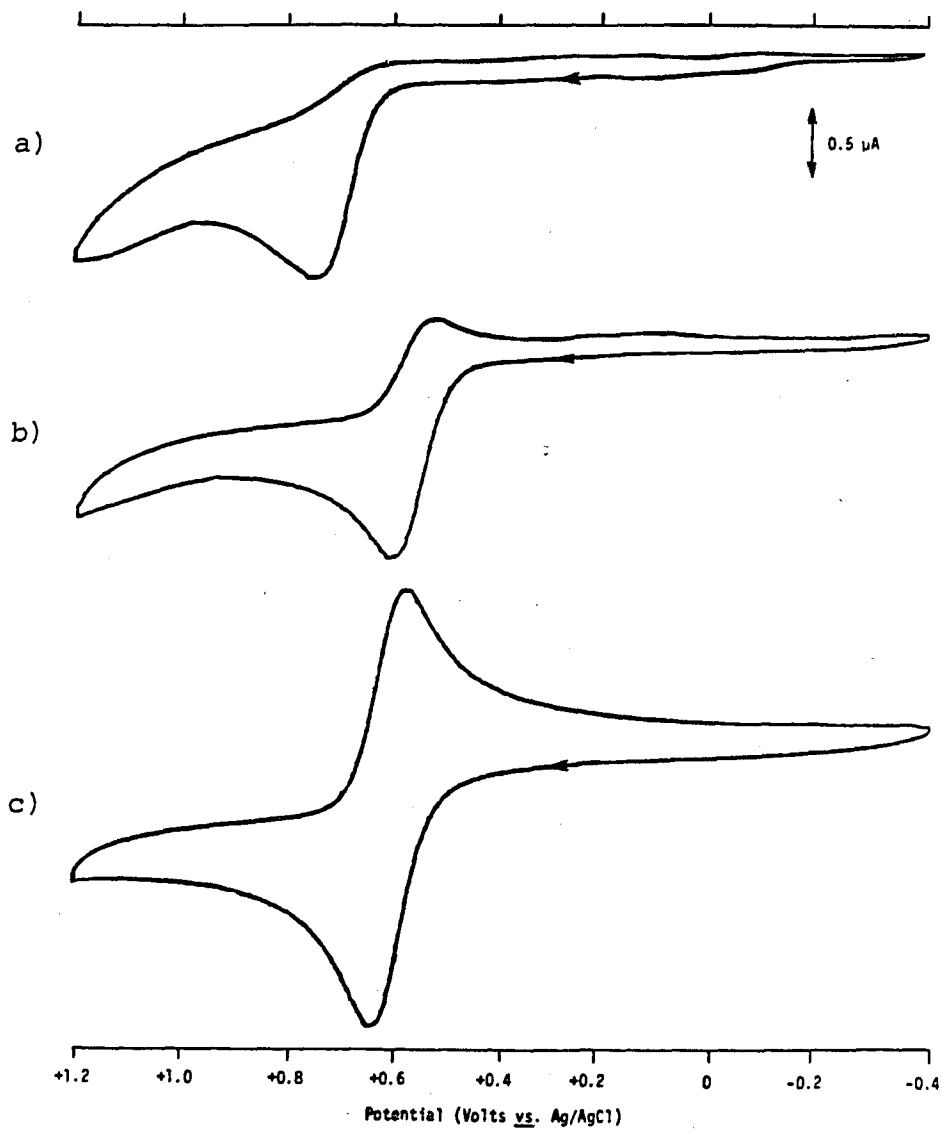
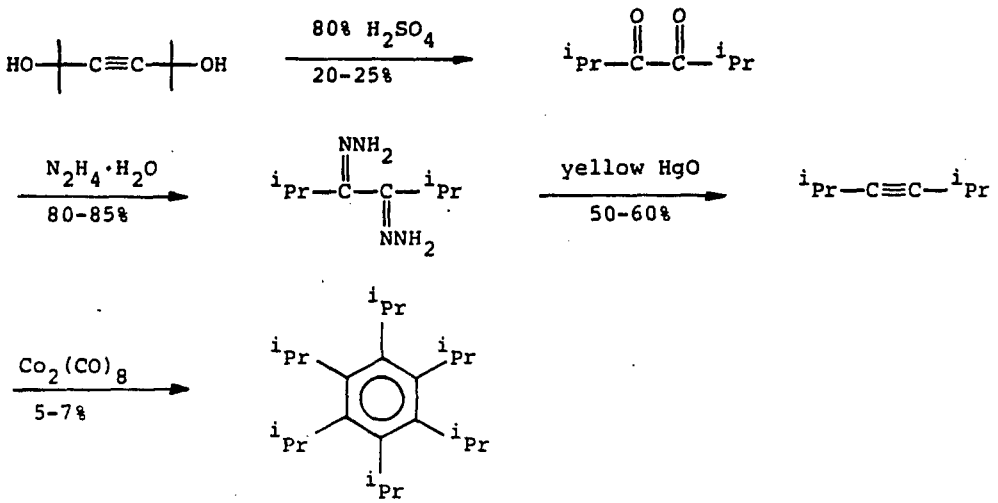


Figure 1. Cyclic voltammograms for 1 mM arene chromium tricarbonyl complexes in CH_3CN at platinum disc electrode, 0.1 M TEAP, 200 mV/sec scan rate. (a) $(C_6H_6)Cr(CO)_3$; (b) $(C_6Me_6)Cr(CO)_3$; (c) $(C_6Et_6)Cr(CO)_3$.

suggested,[9,10] though not conclusively proven, that this stabilization is due to steric inhibition of intermolecular decomposition routes; other reports have stated that electronic effects are responsible for stabilization.[19-21] Indeed, hexamethylbenzene chromium tricarbonyl displays a much more reversible (relative to benzene chromium tricarbonyl) one electron electrochemical oxidation, and the hexaethylbenzene derivative gives rise to a still stabler cation radical (Fig. 1). These results suggest that steric effects are in fact responsible for the stabilization of cation radicals of polyalkylated arene complexes; electronically, little difference would be expected between the hexamethylbenzene and hexaethylbenzene complexes (a fact mirrored by the similarity of the oxidation potentials of the two complexes).

Conclusive demonstration of the importance of steric effects rather than electronic effects as the source of cation stabilization would come from a comparison of two complexes bearing arenes which present comparable steric bulk but dramatically differ electronically. The chromium tricarbonyl complexes of hexaphenylbenzene and hexaisopropylbenzene would be ideally suited for such a comparison. Hexaisopropylbenzene was prepared from 2,5-dimethyl-3-hexyne-2,5-diol (an inexpensive industrial intermediate), as

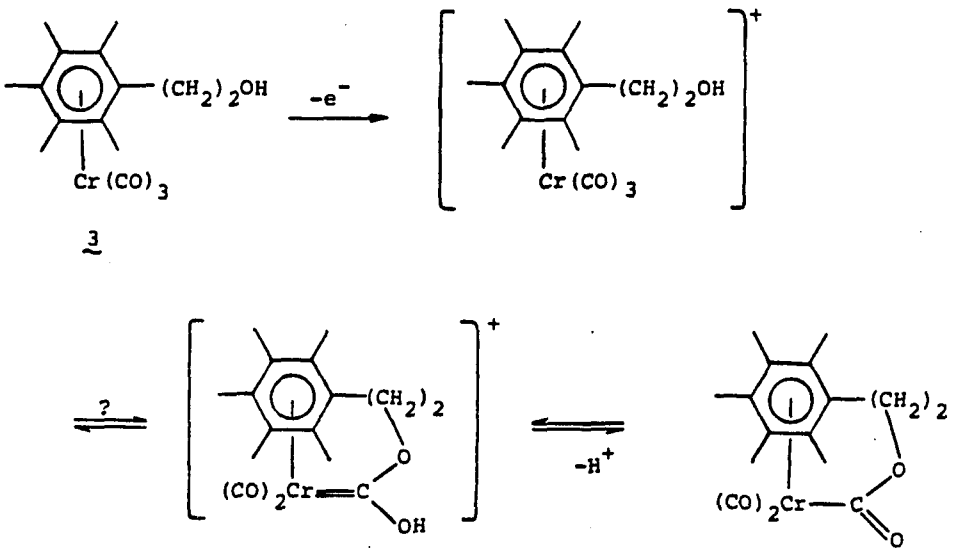
reported by Arnett and Bollinger,[22,23] in a low yield, multistep sequence.



Hexaphenylbenzene was readily prepared from tetraphenylcyclopentadienone and diphenylacetylene.[24] Unfortunately, attempts to form chromium tricarbonyl complexes of these arenes under the usual reaction conditions for such complexation reactions[25] (refluxing butyl ether) led only to the formation of chromium metal. This is an interesting observation, in that in all other cases where arene complexation reactions failed, chromium metal was never formed; intermediate complexation of the highly hindered arenes must generate species which readily lose carbon monoxide under the reaction conditions. Fleeting formation of yellow colors indicative of the presence of arene chromium tricarbonyl complexes was apparent in these reactions, however, and it may prove possible to synthesize the desired arene complexes using recently developed milder techniques for complex formation.[26-28]

Given the encouraging observations on cation radical stabilization discussed above, the chromium tricarbonyl complex of 2-(2,3,4,5,6-penta-

methylphenyl)ethanol was prepared in the hopes of generating a cation of sufficient lifetime to permit intramolecular attack at carbon monoxide by the pendant alcohol.



Chloromethylation of pentamethylbenzene followed by displacement of chloride by cyanide to give 2,3,4,5,6-pentamethylphenylacetonitrile has been reported.[29] Ethanolysis of this nitrile to ethyl 2,3,4,5,6-pentamethylphenylacetate was carried out as reported for the 2,4,6-trimethyl analog.[30] Lithium aluminum hydride reduction of this ester afforded the desired alcohol, and formation of the chromium tricarbonyl complex, 3 (Fig. 2), proved to be routine. In contrast to the hexamethylbenzene chromium tricarbonyl complex, 3 displays a nearly irreversible electrochemical oxidation; scan rates of 2 V/sec or greater are required to observe a reduction wave for the cation radical. For comparison, a 1 mM solution of hexamethylbenzene chromium tricarbonyl qualitatively shows no change in electrochemical behavior even in the presence of 0.285 M ethanol. Thus, intramolecular delivery of the alcohol

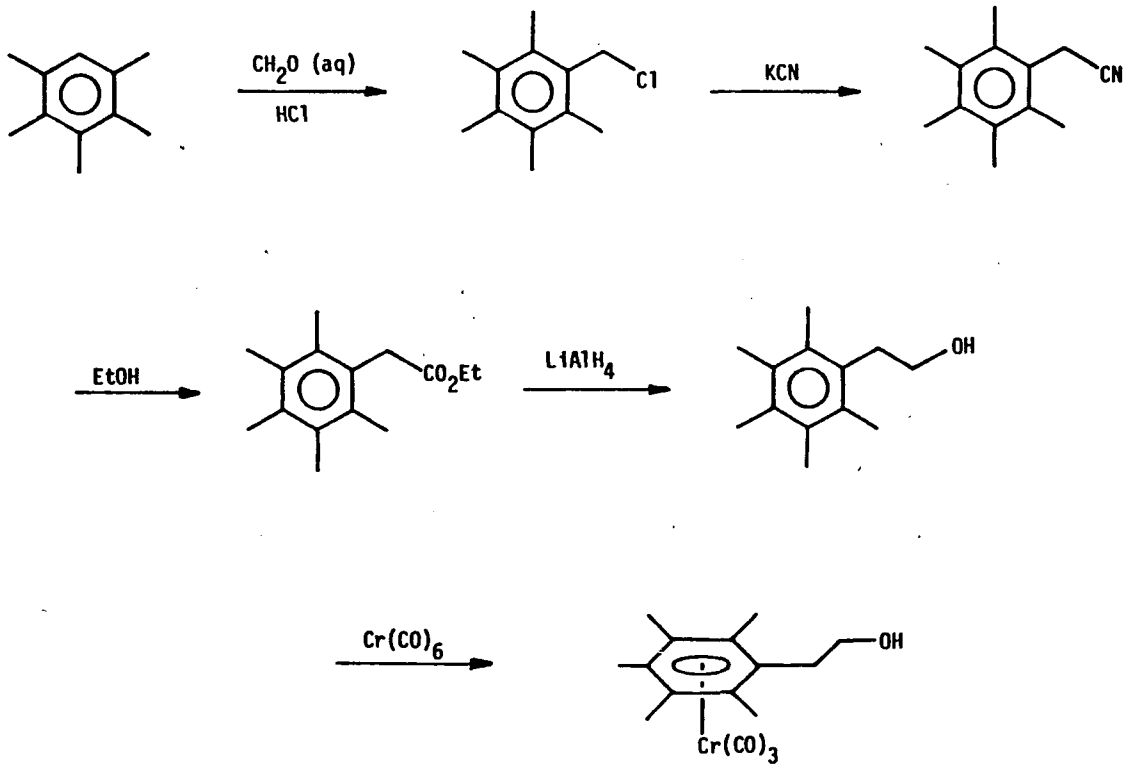
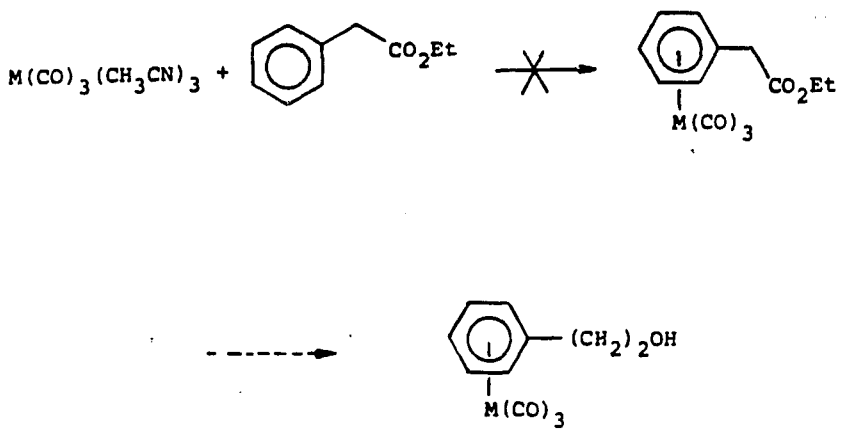


Figure 2. Synthesis of 2-(2,3,4,5,6-pentamethylphenyl)ethanol chromium tricarbonyl (3).

functionality gives rise to a tremendous difference in cation radical reactivity. Bulk electrolysis of **3** results in a multielectron oxidation (n = 1.8), and gas chromatographic analysis of the resulting solution demonstrates the nearly quantitative decomplexation of the arene. (Traces (1-2%) of the corresponding formate -- $HCO_2CH_2CH_2(C_6Me_5)$ -- the product derived from apparent nucleophilic attack by the alcohol at carbon monoxide, were also detected.) The source of this apparently intramolecular quenching of the cation radical by the pendant alcohol functionality is unknown, though it may possibly be due to an entropically-driven (but otherwise sterically inhibited) nucleophilic attack by the alcohol at the metal center (vide infra).

Though cations of arene chromium tricarbonyl complexes which are quite stable on the cyclic voltammetric time scale have been generated, isolation of these cations has not proved possible. Available chemical evidence[19-21] suggests that cations derived from the corresponding molybdenum and tungsten complexes are stabler than their chromium counterparts. Unfortunately, all attempts to prepare the molybdenum and tungsten analogs of complexes **1** and **2** have failed. The direct reaction between phenylethanol and the hexacarbonyls of molybdenum and tungsten, $Mo(CO)_6$ and $W(CO)_6$, under a variety of standard conditions for the formation of arene complexes of these metals[31-33] led to insoluble brown precipitates. Use of the trisacetonitrile complexes, $Mo(CO)_3(CH_3CN)_3$ and $W(CO)_3(CH_3CN)_3$, generally facilitating arene complex formation under milder conditions,[26] gave similar results. Preparation in a two-step sequence involving reduction of intermediate complexes of ethyl phenyl-acetate was thwarted by the inability to form stable complexes of this arene.



Finally, protection of the alcohol as the trimethylsilyl ether permitted the synthesis of minute quantities of the protected molybdenum and tungsten complexes (via the trisacetonitrile complexes), but yields were too low to permit further investigation. Pittman has reported a similar inability to prepare the molybdenum tricarbonyl complex of phenylethanol,[34] and Nesmeyanov has commented on the high thermal instability of the molybdenum and tungsten tricarbonyl complexes of the methyl ether of this alcohol.[35] Despite these difficulties in obtaining functionalized arene molybdenum and tungsten tricarbonyl complexes, the electrochemical oxidation of the known hexamethylbenzene complexes of molybdenum[33] and tungsten[21] tricarbonyl was investigated in the hopes of generating isolable cation radicals.

Hexamethylbenzene molybdenum tricarbonyl appears to be unstable in acetonitrile solution containing 0.1 M tetraethylammonium perchlorate; the initially yellow solution rapidly bleaches, giving a colorless solution displaying a reversible oxidation at +0.3 V. Bulk electrolysis at +0.4 V gives a deep blue solution (characteristic of high-valent molybdenum oxides), but yields an n value of only 0.35; apparently some type of electrocatalytic decomposition

occurs. Qualitatively similar behavior is observed for the 1,3,5-trimethylbenzene molybdenum tricarbonyl complex.[31]

Hexamethylbenzene tungsten tricarbonyl, **4**, is relatively stable in acetonitrile/0.1 M TEAP at room temperature, decomposing only slowly over the course of several hours to generate an unidentified material having a reversible oxidation near 0 V. The cyclic voltammetric behavior of **4**, however, differs remarkably from that of its chromium counterpart. Complex **4** displays a one electron oxidation wave (established by bulk electrolysis) at +0.64 V (near that observed for the chromium analog), but the coupled reduction wave is shifted to near 0 V (Fig. 3a). This splitting is observed even at 0.01 mM concentration, ruling out adsorption effects as the cause.[36] Similar behavior is observed in dimethylformamide (DMF) solvent, though here the reduction wave is shifted nearly 0.6 V more negative than in acetonitrile, and is separated from the oxidation wave by greater than 1.3 V (Fig. 3b). The dependence of the peak potential separation (ΔEp) on scan rate (ν) was determined in both solvents; in each case, plots of ΔEp vs $\nu^{-1/2}$ deviate markedly from linearity (Fig. 4), suggesting that slow electron transfer is not responsible for the observed behavior.[37,38] Thus, it appear that the initially formed cation radical of **4** undergoes some type of follow-up chemical reaction; given the dramatic solvent dependence observed and the rapid rate of this follow-up reaction (no reduction wave is observed at the potential expected for a simple electrochemically reversible redox process even when scanning at 500 V/sec), the reaction would appear to involve some type of ligation of the cation radical by solvent. Thus, oxidation of **4** gives rise to a species incorporating a donor solvent molecule, and this species is more

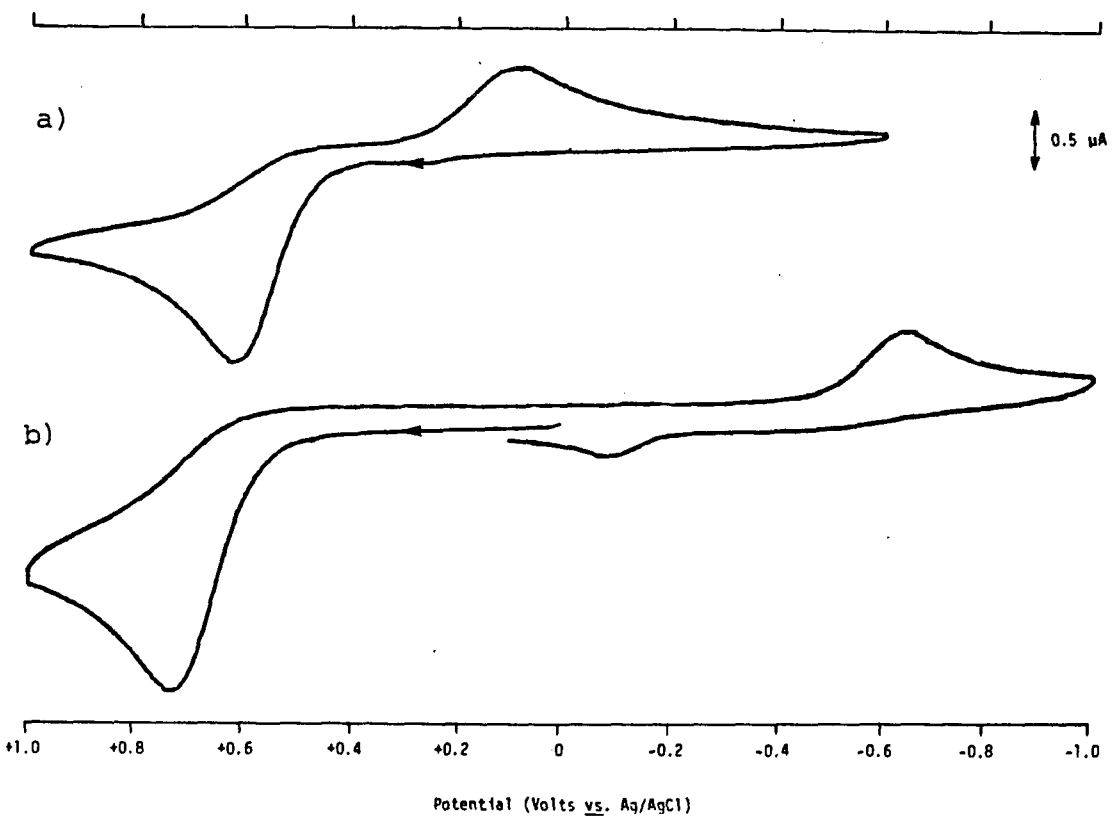


Figure 3. Cyclic voltammograms for 1 mM $(C_6Me_6)W(CO)_3$ (4) at platinum disc electrode, 0.1 M TEAP, 200 mV/sec scan rate. Solvent: (a) CH_3CN; (b) DMF.

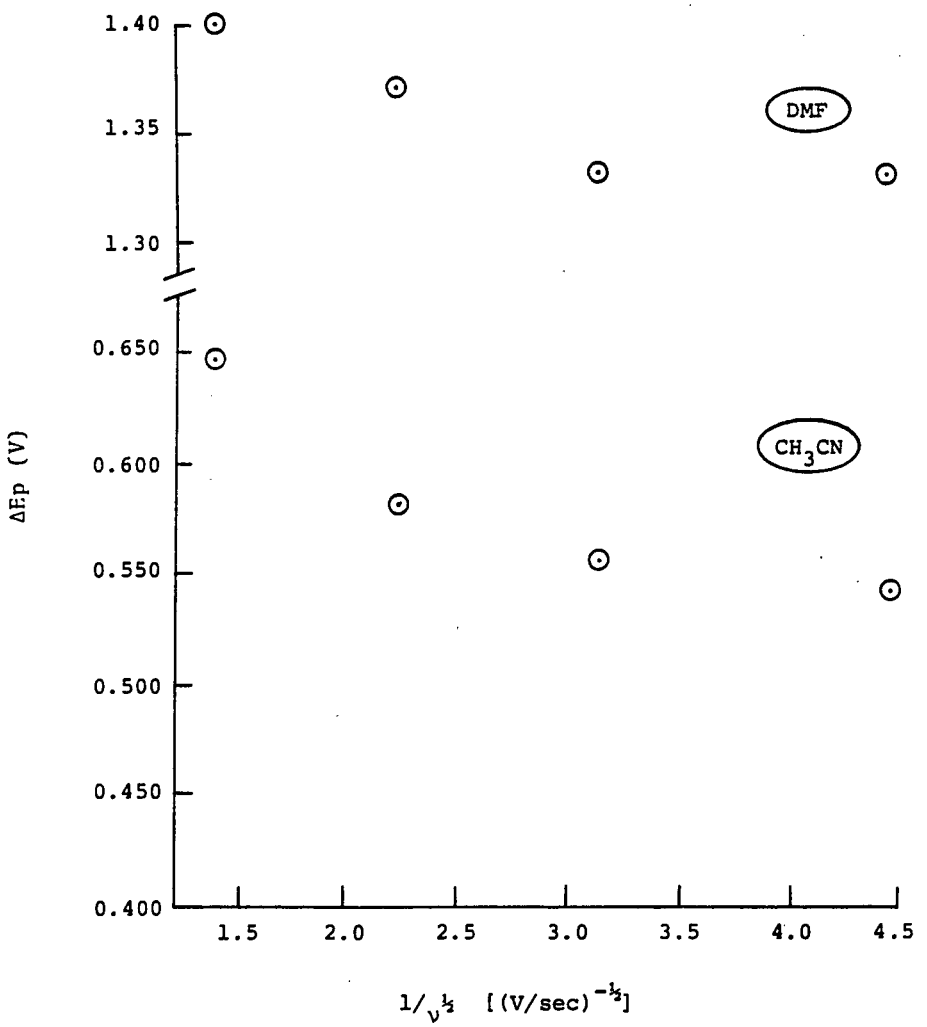
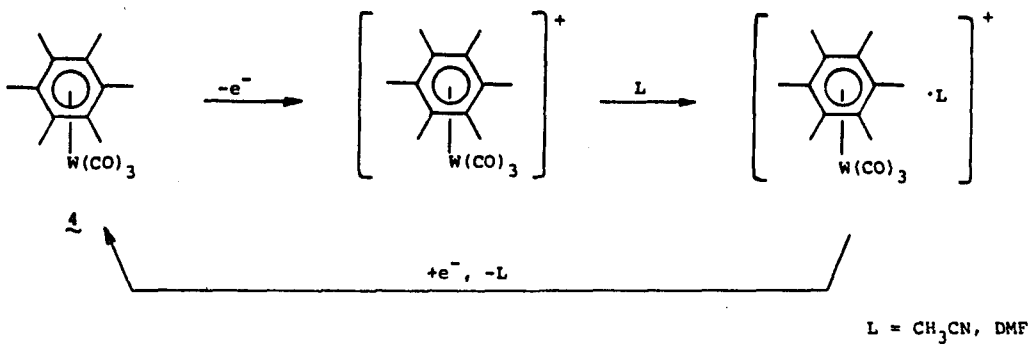
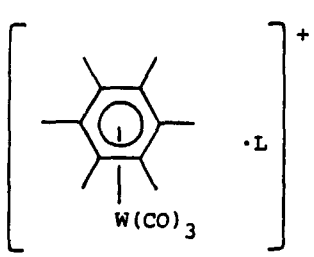


Figure 4. Dependence of peak potential separation (ΔEp) on scan rate (ν) in cyclic voltammetry of $(C_6Me_6)W(CO)_3$ (4) at platinum disc electrode.



difficult to reduce than the unligated cation, resulting in the observed splitting of oxidation and reduction peak potentials. The experimental determination of the structure of this ligated cation is discussed below.

This proposal suggests that addition of other donor ligands to solutions of **4** should give competitive ligation by solvent and by added ligand, and that the observed reduction potentials of the ligated cations should be directly related to the donor ability of the ligands. While the results from triphenylphosphite and triphenylphosphine addition are not conclusive, the shift in reduction potential observed for the oxidized species (Fig. 5) is in accord with that expected; thus, the apparent triphenylphosphine complex, **5a** (bearing a better donor ligand), is more difficult to reduce than the corresponding triphenylphosphite complex, **5b** (bearing a poorer donor ligand).



	L
5a,	PPh_3
b,	$P(OPh)_3$
c,	$P(O^nBu)_3$
d,	$P(^nBu)_3$

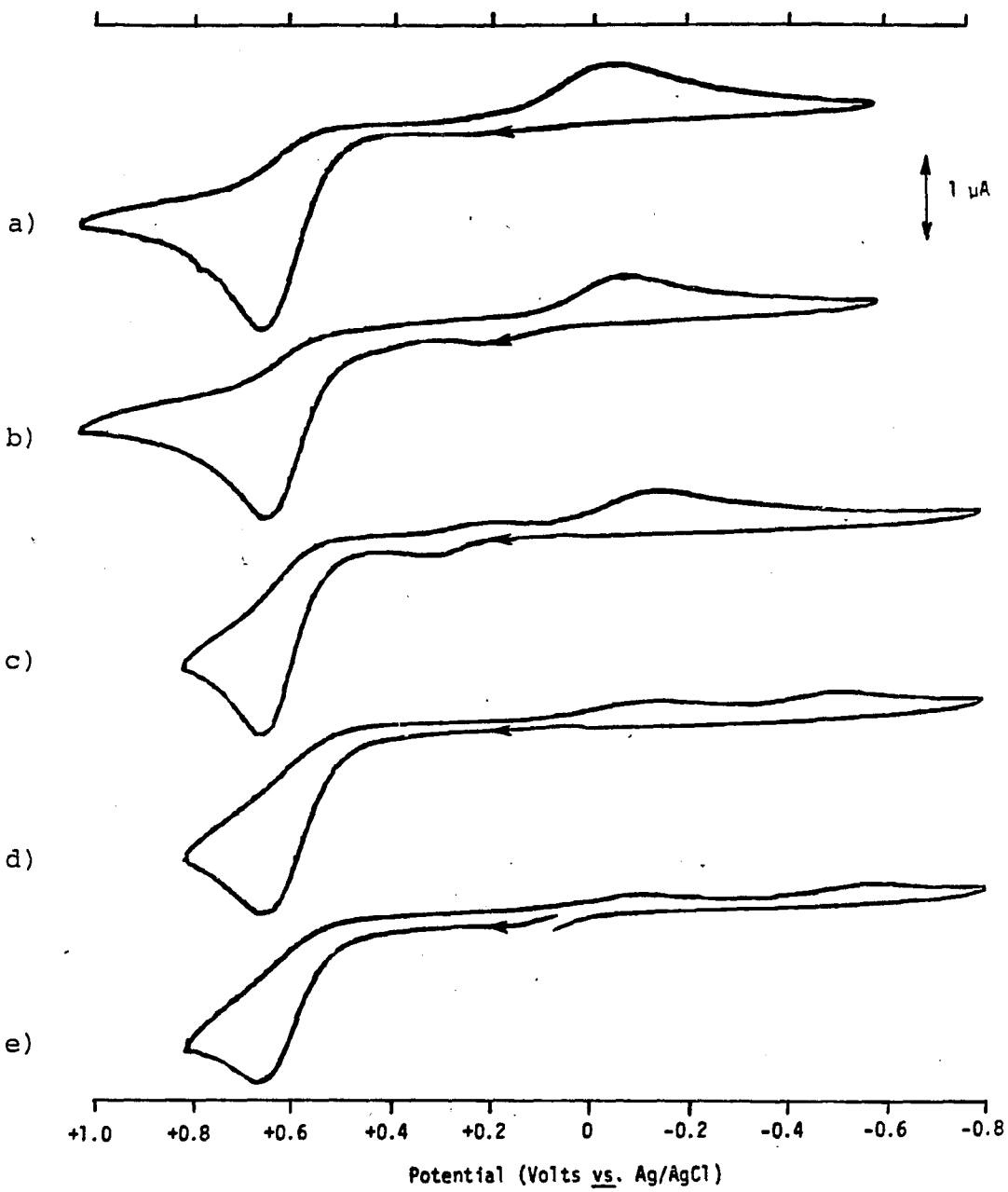


Figure 5. Cyclic voltammograms for 1 mM $(C_6Me_6)W(CO)_3$ (4) in CH_3CN at platinum disc electrode, 0.1 M TEAP, 200 mV/sec scan rate containing (a) no added ligand; (b) 20 mM $P(OPh)_3$; (c) 10 mM PPh_3; (d) 10 mM $P(O^nBu)_3$; (e) 10 mM P^nBu_3.

Addition of tributylphosphite generates two reduction waves; one is due to the acetonitrile adduct of the cation radical of **4**, while the other is apparently due to the tributylphosphite complex, **5c**. Tributylphosphine addition gives similar electrochemical behavior, and here again, the resulting phosphine complex, **5d**, is, as expected, more difficult to reduce than the corresponding phosphite complex, **5c** (Fig. 5). The low reduction currents observed in all cases appear to be due to the instability of the cationic complexes; chemical decomposition of the cation decreases the amount present to be reduced, lowering the current for this reduction.

The results of the incremental titration of **4** with tributylphosphine are presented in Figure 6; the observed behavior is consistent with the proposed rapid intermolecular reaction of the cation radical of **4** with solvent or added ligands. Quantitative analysis of these titration data is not possible due to the complicating effect of relatively rapid decomposition of the cationic complexes. Significantly, in these titration experiments, a new (irreversible) oxidation wave was observed to develop at approximately +0.1 V (Fig. 6). The possibility existed that this wave could arise from oxidation of the phosphine substituted complex, $(C_6Me_6)W(CO)_2(PBu_3)$. Such phosphine substituted complexes, though common for chromium,[39-41] are rare for tungsten; in fact, only one such complex, (mesitylene)$W(CO)_2(PMe_2Ph)$, has been reported.[42] Attempts to prepare $(C_6Me_6)W(CO)_2(PBu_3)$ for comparison were unsuccessful; however, the mesitylene analog, (mesitylene)$W(CO)_2(PBu_3)$ was readily generated, albeit in quite low yield, by the procedure reported by Flood.[42] Mesitylene tungsten tricarbonyl displays electrochemical phosphine titration behavior similar to that of **4**; the new oxidation wave at

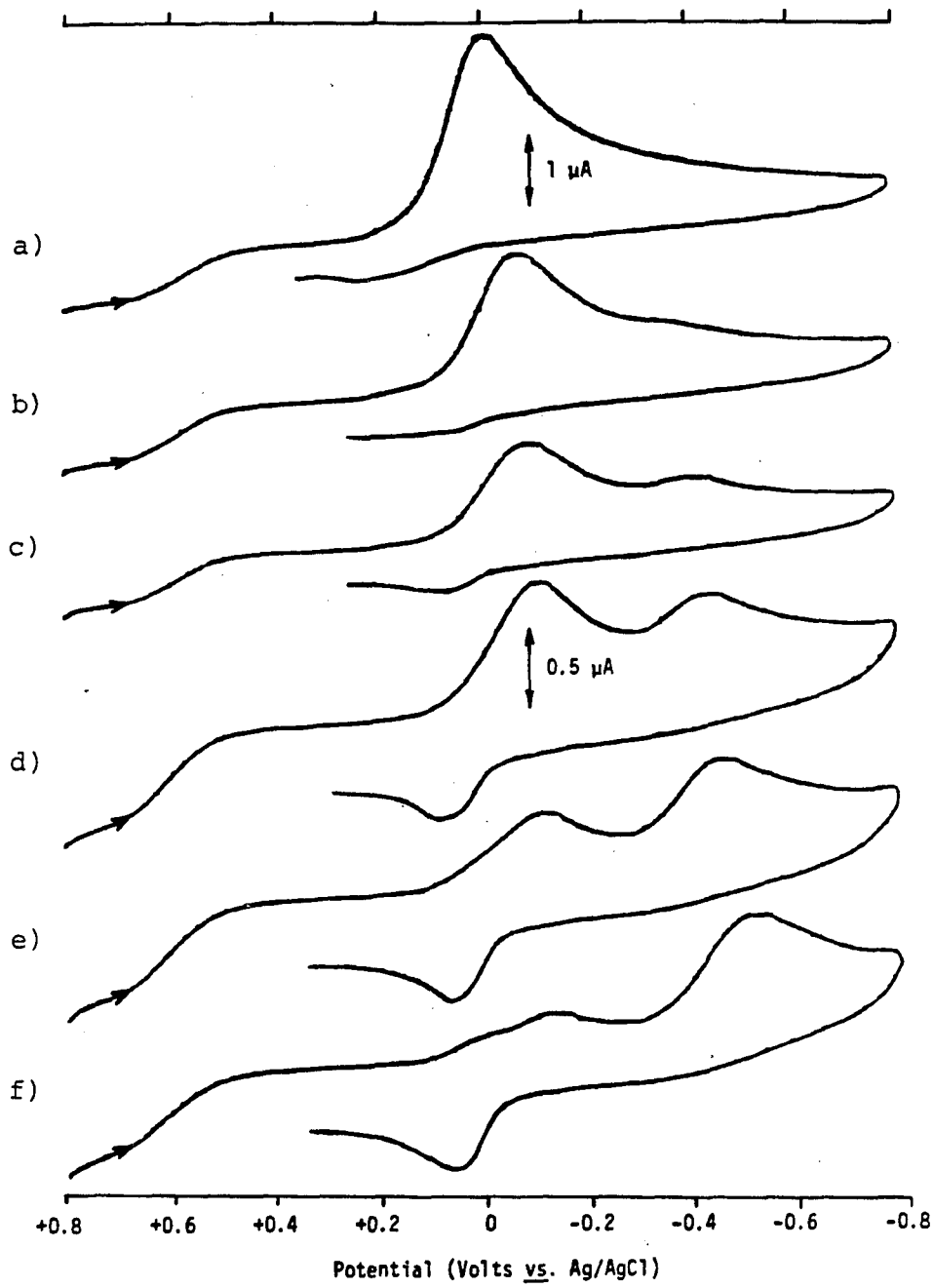
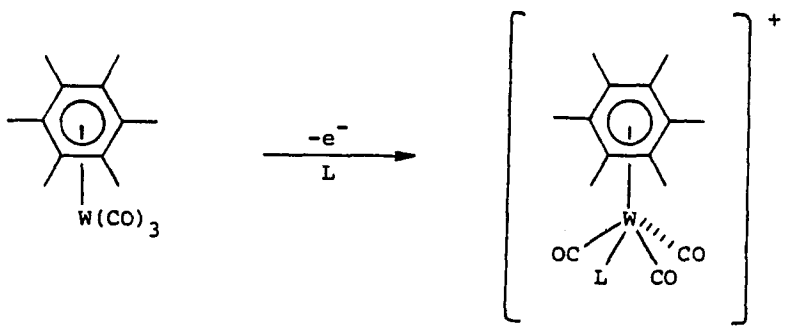


Figure 6. Cyclic voltammograms for 1 mM $(C_6Me_6)W(CO)_3$ (4) in CH_3CN at platinum disc electrode, 0.1 M TEAP, containing (a) no added PBu_3; (b) 0.33 mM PBu_3; (c) 0.67 mM PBu_3; (d) 1.00 mM PBu_3; (e) 1.34 mM PBu_3; (f) 1.67 mM PBu_3. (Held 15 sec at +0.8 V, then scanned at 500 mV/sec.)

approximately +0.1 V, though not as prominent as in the case of **4**, is clearly present. Indeed, (mesitylene)$W(CO)_2(PBu_3)$ displays an irreversible electrochemical oxidation at <u>exactly</u> the same potential as this new oxidation wave. Thus, oxidation of arene tungsten tricarbonyl complexes in the presence of added phosphine, followed by reduction (all on the cyclic voltammetric time scale), leads to formation of the phosphine-substituted complexes. This exceptional facility of ligand substitution in group 6B metal arene tricarbonyl derivatives is unprecedented and strongly implicates direct metal-ligand bonding in the cation radical-ligand adducts (**5**) discussed above. Thus, it seems apparent that these ligand adducts actually represent coordination sphere expansion of the metal in the cationic complexes.



L = CH_3CN, DMF, PR_3, $P(OR)_3$

This coordination sphere expansion of an electrochemically generated cation radical has direct relevance to recent reports on the electrochemical oxidation of organometallic carbonyl complexes. Thus, the electrocatalytic ligand substitutions observed by Kochi,[15] as well as the thermal substitutions in stable organometallic radicals studied by Brown[16] and Trogler,[17] may well proceed <u>via</u> intermediate formation of complexes with increased coordination number (<u>i.e.</u>, the associative mechanism favored by Kochi,[15] Brown,[16] and

Trogler[17] and supported by recently reported[16,17] kinetic investigations).

$$LM(CO)_5 \xrightarrow{-e^-} [LM(CO)_5]^+ \xrightarrow[\text{fast}]{L'}$$

$$[LL'M(CO)_5]^+ \xrightarrow[+e^-]{-L} L'M(CO)_5$$

The electrochemically-driven migratory insertion reaction studied by Giering[43,44]

$$CpFe(CO)_2CH_3 \xrightarrow[CH_3CN]{-e^-,\ +e^-} Cp(CO)(CH_3CN)Fe\overset{O}{\overset{\|}{C}}CH_3$$

may also have its roots in such a phenomenon; in this case, steric crowding in the expanded coordination sphere intermediate may be relieved by rapid insertion of carbon monoxide into the iron-methyl bond.

$$CpFe(CO)_2CH_3 \xrightarrow{-e^-} [CpFe(CO)_2CH_3]^+ \xrightarrow[\text{fast}]{CH_3CN}$$

$$[CpFe(CO)_2(CH_3CN)CH_3]^+ \xrightarrow{\text{fast}} [Cp(CO)(CH_3CN)Fe\overset{O}{\overset{\|}{C}}CH_3]^+$$

$$\xrightarrow{+e^-} Cp(CO)(CH_3CN)Fe\overset{O}{\overset{\|}{C}}CH_3$$

The electrochemical decomposition of simple arene chromium tricarbonyl complexes (vide supra) may also prove to be related; perhaps decomposition is induced by nucleophilic attack at the metal center by solvent[45] (or by the

pendant alcohol in complex 3), and peralkylation of the arene sterically inhibits this attack. In this light, it would be interesting to examine the relative rates of the electrochemically driven migratory insertion reaction in $CpFe(CO)_2CH_3$ and its permethylated analog, $(C_5Me_5)Fe(CO)_2CH_3$; if attack by solvent is sterically inhibited in the methylated analog, the rate of insertion should be slowed relative to the unsubstituted complex. Finally, both the chemical oxidations[7,8] and the photochemical ligand substitution reactions[39-42] of arene metal tricarbonyl complexes may ultimately be mechanistically related to intermediate coordination sphere expansion as well; in the latter case, charge transfer excitation from the metal to the arene could generate local positive charge at the metal and induce associative ligand substitution processes.[46]

Summary and Conclusions

Considerable light has been shed on the mechanism of cation radical stabilization in arene chromium tricarbonyl complexes. The cation radical of hexaethylbenzene chromium tricarbonyl decays much more slowly than that of the hexamethylbenzene complex, rather clearly suggesting steric effects as the primary means of stabilization. In addition, a dramatic effect of intramolecular delivery of an alcohol nucleophile to the electrochemically generated cation radical of an arene chromium tricarbonyl complex has been documented, though the source of the observed destabilization of the cation radical is at present only a matter of conjecture.

The electrochemical oxidation of hexamethylbenzene tungsten

tricarbonyl, **4**, has yielded surprising results which bear direct relevance to current reports on the oxidation of metal carbonyl complexes.[15,43,44,47,48] Oxidation of **4** is followed by rapid complexation of either solvent or added ligands (phosphines or phosphites) to generate expanded coordination sphere intermediates which, when reduced, regenerate **4** or give rise to the ligand-substituted complex. This coordination sphere expansion upon oxidation has far-reaching implications, ranging from support for the proposed associative mechanism for the electrocatalytic substitution of ligands in metal carbonyl complexes[15] and a plausible mechanism for the recently observed oxidatively-promoted migratory insertion of carbon monoxide into a metal-carbon bond,[43,44] to the mechanistically unexplored chemical oxidations of arene metal tricarbonyl complexes and sources of the stabilization of the products of these oxidations. Investigation of the one-electron chemistry of organometallic complexes appears to offer tremendous promise for suggestive and intriguing results of fundamental importance in the field of mechanistic organometallic chemistry and should prove to be an area of vigorous future research endeavors.

Experimental Section

Materials. Organometallic complexes were treated as air sensitive, using standard techniques, until isolated as crystalline solids. Tetrahydrofuran (THF), toluene, and hexane were dried over sodium benzophenone ketyl and vacuum transferred before use. Dichloromethane was dried over CaH_2 and vacuum transferred. Butyl ether was refluxed over $LiAlH_4$ and distilled, under argon, onto Linde 4A molecular sieves. $Cr(CO)_6$, $W(CO)_6$, and $(C_6H_6)Cr(CO)_3$ were obtained from Pressure Chemical Co. (Pittsburgh, PA). Other reagents were purchased from standard commercial sources. E. Merck 70-230 mesh silica gel was used for chromatographic purifications. Hexamethylbenzene molybdenum tricarbonyl,[49] mesitylene molybdenum tricarbonyl,[31] and 2,3,4,5,6-pentamethylphenylacetonitrile[29] were prepared as described. Arene chromium tricarbonyl complexes were prepared using the general procedure described by Mahaffy and Pauson.[25] Mesitylene tungsten dicarbonyl tributylphosphine was prepared as reported by Flood.[42] ^1H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane as an internal standard.

Hydroxyethylbenzene Chromium Tricarbonyl,[32] 1. An argon-flushed, 250 mL three-neck round-bottom flask, equipped with an argon inlet, reflux condenser, and oil bubbler vented in a fume hood (CO evolved!), was charged with 4.0 g $Cr(CO)_6$ (18.2 mmol), 2.17 mL 2-phenethyl alcohol (d = 1.023, 18.2 mmol), 120 mL butyl ether, and 10 mL THF. The colorless suspension was heated to reflux. Reflux was maintained for 72 h, giving a bright yellow solution containing traces of a green solid. The solution was cooled under argon and filtered through a 1" x 2" pad of silica; adhering material was

washed through with a few small portions of THF, leaving a green band on the silica. Removal of solvent in vacuo, with gentle heating, gave an orange oil which solidified to a crystalline mass. Recrystallization from toluene/hexane at 0° C gave long yellow needles, yield 3.1 g (66%), mp 49.7-51.3° C (lit[32] 51-52° C). ^{1}H NMR (acetone-d_6) δ 2.55 (t, 2H, PhC$\underline{H}_2$-), 3.78 (t, 2H, -C$\underline{H}_2$OH), 3.98 (s, 1H, -O$\underline{H}$), 5.3-5.7 (m, 5H, Ph); ^{13}C NMR (acetone-d_6) δ 38.9, 62.8 (-CH_2CH_2-), 92.6, 95.4, 95.8, 113.0 (Ph), 234.7 (CO); IR (THF) ν_{CO} = 1880, 1956 cm^{-1}.

Hydroxypropylbenzene Chromium Tricarbonyl, 2. This complex was prepared as described above, substituting 2.46 mL 3-phenyl-1-propanol (d = 1.008, 18.2 mmol) for phenethyl alcohol. Reflux was continued for 39 h. Crystallization from 35 mL toluene at -50° C afforded 2.95 g (60%) of yellow needles, mp 74.9-76.1° C. ^{1}H NMR (acetone-d_6) δ 1.8 (m, 2H, -CH_2C$\underline{H}_2CH_2$-), 2.5 (m, 2H, PhC$\underline{H}_2$-), 3.6 (broad t, 3H, -C$\underline{H}_2$O$\underline{H}$), 5.6 (m, 5H, Ph); ^{13}C NMR (acetone-d_6) δ 32.1, 34.9, 61.2 (-$CH_2CH_2CH_2$-), 92.4, 94.7, 95.8, 115.7 (Ph), 234.6 (CO); IR (THF) ν_{CO} = 1810, 1880, 1956 cm^{-1}.

Anal. calcd. for $C_{12}H_{12}CrO_4$: C, 52.95; H, 4.44; Cr, 19.10. Found: C, 53.23; H, 4.43; Cr, 18.77.

Hexamethylbenzene Chromium Tricarbonyl.[50] This complex was prepared as described above, substituting 2.95 g hexamethylbenzene (18.2 mmol) for phenethyl alcohol. Reflux was continued for 45 h. The yellow solid which precipitated upon cooling was washed through the pad of silica with THF. Removal of solvents in vacuo afforded a mixture of yellow and white solids. This mixture was washed repeatedly with pentane (6 x 5 mL) to removed unreacted hexamethylbenzene, yielding a bright yellow crystalline

solid, 0.95 g (18%). ^{1}H NMR (CCl_4) δ 2.20 (s); IR (CCl_4) ν_{CO} = 1890, 1960 cm^{-1}.

Hexaethylbenzene Chromium Tricarbonyl.[49] This complex was prepared as described above, substituting 4.48 g hexaethylbenzene (18.2 mmol) for phenethyl alcohol. Reflux was continued for 72 h. Methylene chloride (3 x 10 mL) was used to rinse the silica pad. The volume of the filtrate was reduced to approximately 25 mL in vacuo, with gentle heating. The resulting suspension was filtered, and the solid was washed well with pentane (2 x 10 mL, 5 x 5 mL), affording a bright yellow crystalline solid, yield 1.54 g (22%). IR (THF) ν_{CO} = 1870, 1949 cm^{-1}.

Ethyl 2,3,4,5,6-Pentamethylphenylacetate. A 250 mL round-bottom flask with a magnetic stirrer was charged with 26 mL absolute ethanol, 1.4 mL H_2O, and 8.2 mL concentrated H_2SO_4. With good stirring, 2,3,4,5,6-pentamethylphenylacetonitrile[29] (17.8 g, 0.095 mol) was slowly added, giving a thick suspension. The flask was fitted with a reflux condenser, and the mixture was carefully heated to reflux. Reflux was continued for 20 h, then an additional 0.3 mL H_2O was added to the hot solution (total H_2O 1.7 mL, 0.094 mol). The mixture was cooled, giving a solid tan mass. This was dissolved/suspended in 40 mL $CHCl_3$, washed 2 x 150 mL saturated $NaHCO_3$ and 2 x 200 mL H_2O, and dried over Na_2SO_4. Solvent was removed on a rotary evaporator, giving an off-white solid. This was extracted with 300 mL CCl_4; undissolved solid was removed by filtration. Solvent was removed on a rotary evaporator, and the residue was taken up in 125 mL ethanol and 20 mL H_2O. The mixture was heated and filtered while hot to remove undissolved solids. Finally, the filtrate was heated to boiling, 50 mL H_2O and 30 mL

ethanol were added, and the solution was cooled to room temperature, giving white needles, yield 15.92 g (71%), mp 79.0-80.0°C. ^{1}H NMR (CCl_4) δ 1.24 (t, 3H, $-CH_2CH_3$), 2.19 [s, 15H, $C_6(CH_3)_5$], 3.60 (s, 2H, $ArCH_2-$), 4.06 (q, 2H, $-CH_2CH_3$); IR (KBr) ν_{CO} = 1735 cm^{-1}; ν = 2860-3000 (s, br), 1430-1470 (s, br), 1370 (m), 1340 (s), 1305 (m), 1260 (m), 1215 (s), 1180 (s), 1038 (m), 880 (w), 820 (w) cm^{-1}.

Anal. calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.10, 77.02; H, 9.43, 9.56.

2-(2,3,4,5,6-Pentamethylphenyl)ethanol. Lithium aluminum hydride (2.3 g, 0.074 mol) was suspended in 100 mL anhydrous ether. Ethyl 2,3,4,5,6-pentamethylphenylacetate (11.32 g, 0.048 mol) dissolved in 75 mL ether was added quickly; residues were rinsed in with 2 x 25 mL ether. The suspension was stirred for 15 min, then an additional 0.5 g $LiAlH_4$ (0.016 mol) was added. After stirring for an additional 2 h at room temperature, 100 mL ether was added, and the mixture was carefully quenched with 100 mL ethyl acetate. Filtration on a coarse sintered glass frit afforded a gray solid which was washed with 50 mL ether, 25 mL $CHCl_3$, and 25 mL acetone, then dried in air. This solid was carefully added to 200 mL ice-cold 20% H_2SO_4. The resulting solution was extracted with 2 x 250 mL $CHCl_3$, then 3 x 100 mL $CHCl_3$. The combined organic layers were dried over Na_2SO_4 and K_2CO_3. Solvent was removed on a rotary evaporator, affording a white crystalline solid, 6.36 g (68%), mp 106.6-108.0°C. ^{1}H NMR (CCl_4) δ 1.4 (broad s, 1H $-OH$), 2.2 (s, 9H, $-CH_3$), 2.23 (s, 6H, $-CH_3$), 2.94 (t, 2H, $ArCH_2-$), 3.66 (t, 2H, $-CH_2OH$); IR (KBr) ν = 3200-3400 (s, br), 2880-3000 (s, br), 1400-1500 (s, br), 1040 (s) cm^{-1}.

Anal. calcd. for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.88, 80.93; H, 10.28, 10.17.

2-(2,3,4,5,6-Pentamethylphenyl)ethanol Chromium Tricarbonyl, 3. This complex was prepared as described above, using 2.0 g $Cr(CO)_6$ (9.1 mmol) and substituting 2-(2,3,4,5,6-pentamethylphenyl)ethanol (1.75 g, 9.1 mmol) for phenethyl alcohol. Reflux was continued for 72 h. The silica pad was washed with THF. The volume of the bright yellow filtrate was reduced to approximately 10 mL in vacuo, with gentle heating, giving a yellow solid and a nearly colorless solution. The mixture was filtered, and the solid was washed well with pentane, giving a greenish-yellow solid. This material was chromatographed (in air, collecting in a foil-wrapped receiver) on a 3/4" x 5" column of silica gel slurried in benzene, eluting with benzene/2% acetone. A green band remained on the column; the faster-moving bright yellow band was eluted and immediately brought to dryness in vacuo, affording a bright yellow powder, 2.17 g (73%), mp 113.6-115.5°C (dec). ^{1}H NMR (C_6D_6) δ 0.76 (s, 1H, -OH), 1.59 (s, 6H, $-CH_3$), 1.63 (s, 3H, $-CH_3$), 1.73 (s, 6H, $-CH_3$), 2.36 (t, 2H, $ArCH_2-$), 3.18 (t, 2H, $-CH_2OH$); IR (KBr) νCO = 1860, 1950 cm^{-1}; ν = 3260 (s, br), 2850-3000 (m), 1450 (m), 1390 (s), 1050 (s), 680 (s), 640 (s) cm^{-1}.

Anal. calcd. for $C_{16}H_{20}CrO_4$: C, 58.53; H, 6.14. Found: C, 58.28; H, 6.14.

Hexamethylbenzene Tungsten Tricarbonyl,[21] **4.** A 50 mL Schlenk tube was charged with 15 mL n-decane. The tube was evacuated, then filled with argon. Under an argon flush, 2.146 g $W(CO)_6$ (6.1 mmol) and 0.892 g hexamethylbenzene (5.5 mmol) were added. The tube was then fitted with an

argon-flushed reflux condenser open to a mercury bubbler. The mixture was slowly heated to reflux, with no cooling water flowing; a yellow color developed rapidly. Sublimed $W(CO)_6$ was periodically returned to the solution by shaking the tube. Gentle reflux was continued for 20 h -- a tungsten mirror formed, and some $W(CO)_6$ remained; the solution was yellow. The mixture was cooled and filtered through a 1" x 1" pad of silica under argon, washing with 4 x 10 mL CH_2Cl_2; a black band was left on the silica. Methylene chloride was removed from the bright yellow filtrate in vacuo, giving bright yellow crystals and a colorless supernatant (decane). The mixture was filtered under argon, and the solid was washed with 4 x 10 mL pentane, then dried in vacuo, yield 0.67 g (28%). IR (THF) νCO = 1862, 1943 cm^{-1}.

Apparatus and Procedures. Electrochemical measurements were performed using PAR instruments (EG & G Instrument Co., Princeton, N.J.) and a Houston Instruments x-y recorder or a Tektronix storage oscilloscope. Cyclic voltammetry was carried out in a conventional two-compartment cell in a Vacuum Atmospheres inert atmosphere drybox, using a platinum disc working electrode, at ambient temperature (25 ± 3°C). Potentials were measured and are quoted with respect to a Ag/AgCl reference electrode. Bulk electrolyses were carried out in the same cell using either a platinum foil or a platinum gauze electrode. Solutions were 1 mM in metal complexes and 0.1 M in tetraethylammonium perchlorate. The platinum disc electrode used for cyclic voltammetry was polished on a paper towel after each scan to avoid coating problems, which were especially noticeable with the less-substituted chromium complexes. All solvents and reagents were thoroughly

dried and degassed before use.

Bulk Electrolysis of Hydroxypropylbenzene Chromium Tricarbonyl, 2. Fifteen mL of a 1.09 mM solution of **2** in acetonitrile containing 0.1 M tetraethylammonium perchlorate was electrolyzed at +0.8 V at a platinum gauze electrode. Gas chromatographic analysis of the solution after electrolysis was completed (8-ft 3% SE-52 on Chrom G AWDMCS, 60-200 °C at 15 °C/min, injector 210 °C, detector 230 °C, 35 mL/min flow rate, N_2 carrier) revealed the presence of an approximately stoichiometric amount of 3-phenyl-1-propanol. A solution of complex **2** under analogous chromatogaphic conditions does not generate free arene before electrolysis.

Bulk Electrolysis of 2-(2,3,4,5,6-Pentamethylphenyl)ethanol Chromium Tricarbonyl, 3. Electrolysis of **3**, as above, followed by gas chromatographic analysis (6-ft 3% Carbowax 20 M, 200 °C, injector 260 °C, detector 270 °C, 35 mL/min flow rate, N_2 carrier) revealed the presence of an approximately stoichiometric amount of 2-(2,3,4,5,6-pentamethylphenyl)ethanol and a trace (1-2%) of the corresponding formate (prepared for comparison from the alcohol by overnight reflux in 98% HCO_2H).

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